PB88-113360

International Conference on New Frontiers for Hazardous Waste Management (2nd)
Proceedings of a Conference Held at Pittsburgh, Pennsylvania on September 27-30, 1987

(U.S.) Environmental Protection Agency
Cincinnati, OH

Prepared for

NUS Corp., Pittsburgh, PA

Aug 87

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Hazardous Waste Engineering
Research Laboratory
Cincinnati OH 45268

EPA/600/9-87/018F
August 1987

PB88-113360

Research and Development

EPA

Proceedings:

Second International Conference on New Frontiers for Hazardous Waste Management

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/9-87/018F

2.

3. RECIPIENT'S ACCESSION NO.
PB88 113360/AS

4. TITLE AND SUBTITLE
PROCEEDINGS: SECOND INTERNATIONAL CONFERENCE ON NEW FRONTIERS FOR HAZARDOUS WASTE MANAGEMENT

5. REPORT DATE
August 1987

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
N/A

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
N/A

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Hazardous Waste Engineering Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/9

15. SUPPLEMENTARY NOTES

16. ABSTRACT

ABSTRACT

The International Conference on New Frontiers for Hazardous Waste Management was held in Pittsburgh, Pennsylvania, September 27-30, 1987. The purpose of this conference was to examine the state of technology for the disposal of hazardous waste. Emphasis was placed on the presentation of papers and posters that summarized important new technological developments and concepts with broad international application.

Sessions were held in the areas of : (1) Thermal Destruction, (2) Physical/Chemical Treatment, (3) Biological Treatment, (4) Land Disposal, (5) Solidification, (6) Recycle/Reuse.

These Proceedings are a compilation of the speaker's papers, or abstracts of some, plus scripts of the poster presentations. Where material for the entire work of a presenter was not available for primary publication, copies of the full paper may be obtained in the Conference lobby or later, by contacting NUS Corporation at their Pittsurgh address.

An addition to the 1987 Proceedings is a topical index located at the back of the book, starting on Page 581. We hope you find it useful.

This Conference, as its predecessor, was sponsored by the United States Environmental Protection Agency, NUS Corporation, National Science Foundation, and American Academy of Environmental Engineers.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
Release to Public

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
586

22. PRICE
PCA25/MFA01

EPA Form 2220-1 (9-73)

EPA/600/9-87/018F

SECOND

INTERNATIONAL CONFERENCE

ON

NEW FRONTIERS FOR HAZARDOUS WASTE MANAGEMENT

Proceedings

September 27-30, 1987
Pittsburgh, Pennsylvania

Sponsored by

Hazardous Waste Engineering Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency

NUS Corporation
Pittsburgh, PA

National Science Foundation
Washington, D.C.

American Academy of Environmental Engineers
Annapolis, MD

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

NOTICE

These Proceedings have been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWARD

The managing of hazardous waste has proved itself to be of vast world concern. Because of this, the United States Environmental Protection Agency (U.S. EPA) has developed a keen interest in working with environmental specialists from all nations. We view face-to-face conferences with our peers from many lands to be the most effective method of learning the problems and solutions so important to us all. The papers and poster presentations given at the sessions of this meeting will, we are certain, bring greater understanding of what we must accomplish to return this, our earth, to as close to its primal being as possible. -- At U.S. EPA we feel if we, as world citizens, fail in this mission we will leave a reminder, for future generations, of our dereliction as they suffer the consequences. We must not fail and so we come to this international gathering to learn from the work being done in other lands and to share our own findings.

As one of your hosts, at the Second International Conference on New Frontiers of Hazardous Waste Management, U.S. EPA's Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving the problems posed by hazardous waste in the environment. Its products support the policies, programs, and regulations of U.S. EPA, the permitting and other responsibilities of State and local governments, and the needs of both large and small businesses in handling their wastes responsibly and economically.

These Proceedings present the papers and poster presentation abstracts from this Second International Conference. U.S. EPA, NUS Corporation, National Science Foundation, and Academy of Environmental Engineers have cosponsored this conference in order to summarize important new technological developments and concepts with broad international application.

Thomas R. Hauser
Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

The *International Conference on New Frontiers for Hazardous Waste Management* was held in Pittsburgh, Pennsylvania, September 27-30, 1987. The purpose of this conference was to examine the state of technology for the disposal of hazardous waste. Emphasis was placed on the presentation of papers and posters that summarized important new technological developments and concepts with broad international application.

Sessions were held in the areas of : (1) Thermal Destruction, (2) Physical/Chemical Treatment, (3) Biological Treatment, (4) Land Disposal, (5) Solidification, (6) Recycle/Reuse.

These Proceedings are a compilation of the speaker's papers, or abstracts of some, plus scripts of the poster presentations. Where material for the entire work of a presenter was not available for primary publication, copies of the full paper may be obtained in the Conference lobby or later, by contacting NUS Corporation at their Pittsurgh address.

An addition to the 1987 Proceedings is a topical index located at the back of the book, starting on Page 581. We hope you find it useful.

This Conference, as its predecessor, was sponsored by the United States Environmental Protection Agency, NUS Corporation, National Science Foundation, and American Academy of Environmental Engineers.

ACKNOWLEDGEMENTS

Organizing Board

Allen Cywin
NUS Corporation
Arlington, Virginia

William C. Anderson
American Academy of
Environmental Engineers
Annapolis, Maryland

Ronald D. Hill
U.S. Environmental Protection
Agency
Cincinnati, Ohio

Clyde J. Dial
U.S. Environmental Protection
Agency
Cincinnati, Ohio

Dr. K.T. Thirumalai
National Science Foundation
Washington, D.C.

Organizing Committee

Debra M. Wroblewski
Co-Director
NUS Corporation
Pittsburgh, Pennsylvania

Lynne M. Casper
Co-Director
NUS Corporation
Pittsburgh, Pennsylvania

Peer Review Committee

James Z. Alleman
Purdue University

Gary F. Bennett, Ph.D
The University of Toledo

Arthur Bomberger
NUS Corporation

Donald R. Brenneman
NUS Corporation

Asher Brenner
University of Notre Dame

Alexander H. Danzberger

Robert Fellman
Ebasco Services, Inc.

Brian P. Flynn
ERM- Southwest

Scott C. Fredericks
U.S. EPA

Eugene A. Glysson, Ph.D.
University of Michigan

Michael D. La Grega
Bucknell University

Jack Lindsey
U.S. EPA

Richard Godfrey Luthy
Carnegie Mellon University

Tapan Muhkerjee
National Science Foundation

Tommy E. Myers
USAE Waterways Experiment
Station

Ronald D. Neufeld, Ph.D.
University of Pittsburgh

E. Timothy Oppelt
U.S. EPA

Frederick G. Pohland, Ph.D.
Georgia Institute of
Technology

F. Michael Saunders, Ph.D.
Georgia Institute of
Technology

William B. Schmidt
U.S. Department of
Interior

Norbert B. Schomaker
U.S. EPA

Randy Seeker
U.S. EPA

William Shively
CH_2M Hill

Gerald H. Teletzke, Ph.D.
GHT Associates

J.C. Touhill
Baker/TSA, Inc.

Thomas Voltaggio
U.S. EPA

Carlton Wiles
U.S. EPA

CONTENTS

Page

Notice ii
Foreward iii
Abstract iv
Acknowledgements v

Paper Number (The index, at the back of this volume, will refer to the individual Paper Numbers indicated below for each paper presented.)

SESSION 1 - THERMAL DESTRUCTION

1. Nonsteady-state Testing of Industrial Boilers Burning Hazardous Wastes
Carlo Castaldini, Harold Lips, Ramsay Chang, Acurex Corporation; and Ivars Licis, U.S. Environmental Protection Agency 1

2. Waste Destruction by Plasma Arc Pyrolysis
Michael F. Joseph, Westinghouse Plasma Systems Canada Inc.; and Thomas G. Barton, Pyrolysis Systems Incorporated 11

3. Leaching Characteristics of Residual Ashes From the Incineration of Municipal Solid Waste
Tracey L. Clapp, David S. Kosson, Robert C. Ahlert, Rutgers University, Department of Chemical and Biochemical Engineering 19

4. The Clean-up of Contaminated Soil by Thermal Desorption
JoAnn S. Lighty, David W. Pershing, Chemical Engineering Department, University of Utah; Vic A. Cundy, Frank R. Groves, Jr., Departments of Mechanical and Chemical Engineering, Louisiana State University; and David G. Linz, Environment and Safety Research, Gas Research Institute 29

5. High Temperature Slagging Incineration of Hazardous Waste
Rik Vanbrabant, and Norbert Van de Voorde, Waste Treatment Department, Belgian Nuclear Research Center (SCK/CEN) 35

6. PCB Trial Burn in a Modular, Movable Incinerator
Prakash Acharya, ENSCO Environmental Services (ENSCO) 43

Preceding page blank

SESSION 2 - PHYSICAL/CHEMICAL TREATMENT

7. Extractive Methods for Soil Decontamimation; Operational Treatment Installations in the Netherlands
J.W. Assink, Dutch Organization for Applied Scientific Research (TNO) 55

8. Evaluating Elector-Kinetics as a Remedial Action Technique
Jao-Jia Horng, Sunirmal Banerjee, Department of Civil Engineering, University of Washington; and Jonathan G. Herrmann, U.S. Environmental Protection Agency 65

9. Offsite Treatment of RCRA Hazardous Wastes - A Case Study
Ronald J. Turner, U.S. Environmental Protection Agency 79

10. The Destruction of Hazardous Organic Waste Materials Using the MODAR Oxidation Process
Carl N. Staszak, Kenneth C. Malinowski, CECOS International, Inc.; and William R. Killilea, Kathleen C. Swallow, MODAR, Inc. 97

11. Remedial Action of Hydrocarbon Contamination in the Glacial Drift Deposit
Jan Wilk and Wladyslaw Skalny, Development Center for Chemical Raw Materials in Cracov, Poland 107

12. Prospects for Robotics in Hazardous Waste Management
James F. Osborn, William W. Whittaker, and Syd Coppersmith, Field Robotics Center, The Robotics Institute, Carnegie Mellon University 119

SESSION 3 - BIOLOGICAL TREATMENT

13. Evaluation of an Engineered Biodegradation Land Treatment System for Soil Decontamination at a Wood Preserving Site
Jaw K. Fu and John R. Smith, Keystone Environmental Resources, Inc. 129

14. Stimulation of Microbial Biodegradation in a Jet Fuel Contaminated Soil
Raymond N. Yong and Diana Mourato, Geotechnical Research Centre, McGill University 131

15. Biological Treatment of Hazardous Aqueous Wastes
Edward J. Opatken, Hinton K. Howard, and James J. Bond, U.S. Environmental Protection Agency 148

16. Feasibility Study on Disposal of Oily Sludge in Kuwait
Amin S. ElNawawy, Fikry H. Ghobrial, and Abdelghani A. Elimam, Kuwait Institute for Scientific Research 162

17. Treatment of Toxic Wastewaters by Powdered Activated Carbon
John Meidl, ZIMPRO/PASSAVANT INC. 170

SESSION 4 - LAND DISPOSAL

18. The Attenuation of Landfill Gas Odour Using Waste Materials
J.R. Emberton, P.E. Scott, and C.G. Dent, Environmental Safety Centre, AERE Harwell 172

19. Plastic Concrete Slurry Trench Cutoff Walls
Jeffrey C. Evans, Bucknell University; Eric D. Stahl, R.H. Stahl & Sons, Inc.; and Eric Drooft, Sardone Construction Co. 185

20. Study of Transport of Concentrated Organics in the Unsaturated Zone
Tissa H. Illangasekare, University of Colorado; and Danny D. Reible, Louisiana State University 193

21. Worldwide Perspective on the Disposal of Solid Wastes from Mining Operations
Jacek S. Libicki, POLTEGOR 205

22. Distribution of Flow Rates and Tracer Breakthrough Times in Field Soil
Andrew S. Rogowski, USDA-ARS, Northeast Watershed Center 219

SESSION 5 - BIOLOGICAL TREATMENT

23. Stabilization of Enzymes Used to Degrade Pesticides
Daniel R. Coleman, F. Reese Frazer, Douglas B. Rivers, Thomas R. Tice, Thomas O. Dappert, and David W. Mason, Southern Research Institute 231

24. Plant Responses to Petrochemical Wastes
Robert W. Duell and Fred E. Katz, New Jersey Agricultural Experiment Station 237

25. Stimulated In Situ Biodegradation of Aromatic Hydrocarbons
Peter Geldner, Associate Consultant Engineer 247

26. Bacterial Treatment of PCB-Contaminated Soils: Prospects for the Application of Recombinant DNA Technology
Ronald Unterman, frank J. Mondello, Michael J. Brennan, Ronald E. Brooks, David P. Mobley, John B. McDermott, and Charles C. Schwartz; General Electric, Corporate Research and Development 259

27. Screening Study for On-Site Biological Remediation of Soils Contaminated by Coal Conversion Residuals and By-Products
A. Brenner, R.L. Irvine, L.H. Ketchum, Jr., and C.F. Kulpa, Jr., University of Notre Dame; and J.P. Moreau, Niagra Mohawk Power Corporation 265

28. White Rot Fungus Detoxification Research: Status and Directions
John A. Glaser and Pasquale R. Sferra, U.S. Environmental Protection agency 277

SESSION 6 - SOLIDIFICATION

29. Ocean Disposal of Solidified/Stabilized Hazardous Wastes
Paul L. Bishop and Kristine L. Melchinger, Department of Civil Engineering, University of New Hampshire 285

30. Soluble Silicates in Solidification and Fixation Technology
Jesse R. Conner, Conner Technologies 295

31. In Situ Vitrification - an Innovative Thermal Treatment Technology
V.F. FitzPatrick, C.L. Timmerman, and J.L. Buelt, Pacific Northwest Laboratory 305

32. Characterization and Treatment of Wastes Comprised of Hazardous, Radioactive Mixed, and Rransuranic Fractions
James T. Nelson and Richard A. Martineit, NUS Corporation; and R.E. Helms, Martin Marietta Energy Systems, Inc. 323

33. A Method for Predicting Quality in Solidified Hazardous Wastes
C.G. Dent, P.E. Rushbrook, and G. Baldwin, Waste Research Unit Harwell Laboratory 331

34. Interlaboratory and Intralaboratory Reproducibility of Results of an Investigation of Test Methods for Solidified Waste Characterization
J. Stegeman, Environment Canada, Conservation and Protection Wastewater Technology Centre 341

SESSION 7 - THERMAL DESTRUCTION

35. The Generation of Hazardous Waste by MSW-Incineration Calls for New Concepts in Thermal Waste Treatment
Paul H. Brunner and Peter Baccini, Swiss Federal Institute for Water Resources and Water Pollution Control 343

36. Incineration of PCB's in France: Decontamination of Electrical Equipment and Polluted Sites
G. Millot, PECSIE; and Georges Milleret, TREDI 351

37. Engineering Analysis of Metal Emissions from Thermal Destruction Devices
R.G. Barton, W.D. Clark, W.R. Seeker, Energy and Environmental Research Corp.; and C.C. Lee, U.S. Environmental Protection Agency 359

38. Distillation of Leachates from Hazardous Waste Landfills - One Year of Experience
Hans-Christian Steinmetzer, Bavarian EPA 367

39. Pilot-Scale Incineration of a Dioxin-Containing Material
Larry R. Waterland, Robert W. Ross, II, Thomas H. Backhouse, Ralph H. Vocque, and Johannes W. Lee, Acurex Corporation; and Robert E. Mournighan, U.S. Environmental Protection Agency 375

SESSION 8 - PHYSICAL/CHEMICAL TREATMENT

40. Supercritical Fluid Extraction and Catalytic Oxidation of Toxic Organics from Soils
Kerry M. Dooley[1], Robert Gambrell[2], and F. Carl Knopf[1], Department of Chemical Engineering[1], and Department of Marine Science[2], Louisiana State University 383

41. EPA's Pilot Scale Treatability Studies for Hazardous Wastes
Robert A. Olexsey and Douglas W. Grosse, U.S. Environmental Protection Agency 399

42. The Use of Air Stripping and Vapour Phase Adsorption Processes for the Removal of Volatile Organics from Contaminated Grounwater
L. Simovic[1], L.A. Lishman[2], and S.A. Zaidi[1]; [1]Environment Canada, and [2]McMaster University 409

43. Chemical Destruction of Chlorinated Dioxins and Furans
Charles J. Rogers and Alfred Kornel; U.S. Environmental Protection Agency 419

44. Supercritical Extraction of Contaminants from Water and Soil with Toxicological Validation
T.R. Irvin[2], E.K. Stevens[2], R.K. Roop[1], and A. Akgerman[1]; [1]Department of Chemical Engineering, and [2] Department of Veterinary Anatomy; Texas A&M University 425

SESSION 9 - POSTERS

45. Durability of Slurry Cut-Off Walls Around The Hazardous Waste Sites
Raj P. Khera, Department of Civil and Environmental Engineering, New Jersey Institute of Technology; Yuan H. Wu, Dames and Moore: M. Khalid Umer, Department of Civil Engineering, New Jersey Institute of Technology 433

46. Assessment of Leachate Monitoring and Toxicity in Groundwater Around Iowa Municipal Landfills
Burton C. Kross, Department of Civil and Environmental Engineering, and Department of Preventive Medicine and Environmental Health, University of Iowa 441

47. Leachate Synthesis for Clay and FML Compatibility Testing
Stephen S. Odojewski, Water Resource Associates, Inc. 451

48. Minimization of Waste Utilizing High Pressure Membrane Filter Presses
C. Robert Steward, Schriver Filter Presses/Eimco Process Equipment Company 459

SESSION 10 - LAND DISPOSAL

49. Soil Standards for Hazardous Waste Disposal and Cleanup in the Netherlands
F.B. DeWalle, University of Washington 461

50. Land Treatment of an Oily Waste - Degradation, Immobilization and Bioaccumulation
Raymond C. Loehr, The University of Texas; John H. Martin, Jr., Cornell University; and Edward F. Neuhauser, Niagara Mohawk Power Corporation 469

51. The Use of Contaminated Material for the Creation of New Housing Land at Thamesmead, London
George W. Lowe, London Scientific Services 477

52. Secure Landfill Design/Operation to Reduce Leachate and Closure Cost
Randolph W. Rakoczynski, Waste Resource Associates, Inc. 485

53. Safe, Zero-Migration Ultimate Disposal of Solid Hazardous Waste in Salt Caverns
H.-J. Schneider, Kavernen Bau- und Betriebs-GMBH; and W. Bishop, PB-KBB Inc. 493

54. In Situ Treatment Process for Removal of Volatile Hydrocarbons from Soils: Results of Prototype Test
Phillip N. La Mori and Michael Ridosh, Toxic Treatments (USA) Inc. 503

SESSION 11 - RECYCLE/REUSE

55. The One-step Method for Recovery and Reuse of Waste Chromium from Electroplating Plants
Yancey Chou, The Peoples Republic of China 511

56. Reuse of Waste Ferrous Sulphate
Lucjan Pawlowski and Marek Kotowski, Department of Water and Wastewater Technology, Technical University of Lublin 521

57. Barium Recovery From Spent Hardening Salts
Ryszard Szpadt and Marta Sebastian, Institute of Environment Protection engineering, Technical University of Wroclaw 531

58. Economic Evaluation of Source Reduction Projects
David Butler, Carl Fromm, and Christopher Timm, Jacobs Engineering Group Inc. 539

59. Minimization of Solvent Wastes from an Electronic Capacitor Manufacturing Process
Harry M. Freeman, U.S. Environmental Protection Agency; James R. Teuscher, SFE Technologies, Inc.; Michael S. Callahan, and Carl H. Fromm, Jacobs Engineering Group, Inc. 547

SESSION 12 - POSTERS

60. Selection of a Mobile Incineration System
John C. Reed, Steven R. Strauss, and James D. Cobb, Illinois Environmental Protection Agency 555

61. Tracing Contaminant Leaks Using Borehole Television
Alan M. Jacobs, GEOPROBE 561

62. The Effect of pH on 2,4-D Biodegradation
G.L. Sinton, L.E. Erickson, and L.T. Fan, Department of
Chemical Engineering, Kansas State University 573

INDEX 581

NONSTEADY-STATE TESTING OF INDUSTRIAL BOILERS BURNING HAZARDOUS WASTES

Carlo Castaldini, Harold Lips, and Ramsay Chang
Acurex Corporation
Environmental Systems Division
485 Clyde Avenue
P.O. Box 7044
Mountain View, California 94039
and
Ivars Licis
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
26 West St. Clair Street
Cincinnati, Ohio 45268

ABSTRACT

Results from several field tests of industrial boilers burning liquid hazardous waste have indicated that these devices achieve destruction and removal efficiency (DRE) of principal organic hazardous constituents (POHC) in excess of 99.99 percent when operating under typical steady-state combustion conditions. Recent EPA-sponsored field tests have focused on the effect of nonsteady-state and transient boiler operation on DRE and formation of products of incomplete combustion (PICs) from decomposition, recombination, or partial oxidation of the parent POHC. This paper presents test results on three industrial boilers cofiring liquid wastes spiked with hazardous organic compounds. The boilers tested comprise the major watertube design types: one gas- and oil-fired packaged boiler, one field-erected gas-fired boiler, and one coal-fired stoker. Emission sampling included detailed evaluations of volatile and semivolatile organic pollutants in the flue gas for POHC, DRE, and PIC determinations under several steady conditions and induced operational upsets. In the case of the coal-fired stoker, emission evaluations also included detailed organic and metal analyses of flue gas and flyash samples from collection devices.

INTRODUCTION

Cofiring of combustible hazardous wastes with conventional fuels in industrial boilers is widely practiced in industry as an economical disposal method and for energy recovery. The Environmental Protection Agency (EPA) Office of Solid Waste and Emergency Response has conducted a regulatory impact assessment to evaluate hazards and potential control measures in preparation for recommending a boiler regulation. To support this regulatory assessment, EPA's Hazardous Waste Engineering

Research Laboratory and Office of Solid Waste and Emergency Response conducted a series of field tests, Sites A through K, to evaluate the capability and limitations of industrial boilers for hazardous waste thermal destruction by cofiring with conventional fuels (1). While these tests showed high waste destruction (composite weighted DRE of 99.998 percent), the tests were conducted at nominally steady operating conditions and did not address transient and off-design operating conditions which may influence DRE. To complete this evaluation, information was then needed on boiler operational limits yielding satisfactory waste destruction, and on the effects of routine, nonsteady operation on destruction performance.

PURPOSE

The overall objective of this study was to quantify DREs of POHCs for transients and off-design operating conditions during cofiring in industrial boilers. The study was also to provide sufficient DRE data to deduce an acceptable operating window, and background information for determining regulatory requirements for organic, metal, and chloride emissions during cofiring of hazardous wastes.

APPROACH

Three watertube boilers were selected for these tests. Table 1 summarizes design characteristics and test operating conditions for these boilers.

Site L is a forced draft Combustion Engineering (CE) package watertube boiler with a maximum rated capacity of 13.9 kilograms per second (kg/s) (110,000 pounds per hour (lb/hr)) of superheated steam. Natural gas and/or No. 6 oil is fired through a single dual air register burner. The burner is retrofitted with two steam atomized liquid waste guns designed to fire a distillation byproduct containing methylmethacrylate (MMA). The waste was spiked with CCl_4 and monochlorobenzene in concentrations ranging from 0.7 to 4.5 percent by weight. MMA concentration varied from 6 to 8.4 percent by weight. Spiked waste feedrate during tests accounted for 7.3 to 56 percent of the total heat input to the boiler. This waste feedrate encompasses the range of typical plant operating practice of 15 to 40 percent of the total heat input. Boiler loads tested were as low as 25 percent of capacity which is lower than normal operating practice for this site. In addition to tests performed at high- and low-steam loads, excess air levels, and waste/fuel ratios, several other conditions were investigated including transients, waste atomization upsets, and sootblow cycles.

Site M is a field-erected CE watertube boiler with a rated capacity of 44 kg/s (350,000 lb/hr) of superheated steam. The boiler is equipped with four gas and/or oil-fired CE R-type burners arranged in a square pattern. Combustion air is preheated to about 260°C (500°F). Typically, the boiler operates at about 57 percent capacity using a mixture of natural gas, waste process gas, and a liquid waste. This waste, fired with the lower 2 burners, consists of heavy ends from a butanol/propanol production unit combined with surface oil from a waste retention pond. During the tests, the waste oil was spiked with CCl_4, monochlorobenzene, and 1,2,4-trichlorobenzene in varying concentrations ranging from 1 to 15 percent by weight. The boiler was tested at nominal- and low-steam load conditions with various amounts of excess

Table 1. Boiler design and operating characteristics.

				Operation					
Site identification	Boiler* type and capacity kg/s (10^3 lb/hr)	Primary fuel	Waste fuel POHC†, metals	Steam load kg/s (10^3 lb/hr)	Percent O_2	POHC concentration (percent)	Waste/primary fuel percent heat input	Additional variables	Sampling protocol
L	FD-WT 1 burner 14 (110)	No. 6 oil	TSB CCl_4,MCB,MMA	3.4 to 7.8 (27 to 62)	2.5 to 7.9	2.8 to 7.5	7.3 to 34	Load and O_2 transients; waste flow transients; atomization; sootblow	Continuous monitors, mini-VOST, periodic full-VOST
		Natural gas	TSB CCl_4,MCB,MMA	3.2 to 9.6 (25 to 76)	1.2 to 7.5	0.7 to 8.4	8.8 to 56	Load and O_2 transients; waste flow transients; atomization; sootblow	Continuous monitors, mini-VOST, periodic full-VOST
M	FD-WT 4 burners 44 (350)	Natural gas	Waste oil CCl_4,MCB, 1,2,4-TCB	16 to 25 (125 to 195)	1.2 to 10	1.0 to 15	20 to 30	Waste lightoff; waste injection location; waste flow transients; atomization; sootblow	Continuous monitors, mini-VOST, periodic full-VOST
N	BD-WT Stoker 19 (150)	Stoker coal	Sludge TCE;1,2,4-TCB Pb,Cr	10 to 17 (80 to 135)	6.7 to 10	5 to 10	0	None	Continuous monitors, mini-VOST, periodic full-VOST, EPA MM5, Andersen, ash sampling
		Stoker coal	No. 2 oil TCE;1,2,4-TCB Pb,Cr	10 to 17 (80 to 135)	5.4 to 12	5 to 6	20 to 35	None	

*FD-WT = forced draft watertube; BD-WT = balanced draft watertube.

†TSB = third stage bottoms from production of methyl methacrylate (MMA); CCl_4 = carbon tetrachloride; MCB = monochlorobenzene; TCE = trichloroethylene; 1,2,4-TCB = 1,2,4-trichlorobenzene.

air. Nonsteady and upset test conditions were induced by operating the boiler with extreme high and low excess air and during wasteflow transients, waste lightoff, waste atomization cutoff, and sootblow cycles. A less favorable waste injection location was also tested by switching waste firing to the upper two burners. This caused very unstable combustion conditions with significant smoke generation.

Site N is a Riley balanced-draft spreader stoker with a rated capacity of 19 kg/s (150,000 lb/hr) of saturated steam. Figure 1 illustrates a side view of the boiler and flyash control devices. The boiler disposes of liquid sludge through two pressure atomized guns located opposite each other in the furnace side wall at approximately 3 feet (ft) above the grate. The sludge, consisting primarily of water (greater than (>) 90 percent), was spiked with various quantities of trichloroethylene and 1,2,4-trichlorobenzene for a total sludge concentration of 5 to 10 percent by volume. Lead and chromium salts in water solution were also injected to determine the partitioning of these metals among the bottom ash, dust collector ash, or baghouse ash. Boiler test loads and excess air levels spanned the range of the plant operating practice. Excess air in the furnace was varied by changing undergrate and overfire airflows. Similar tests were also performed

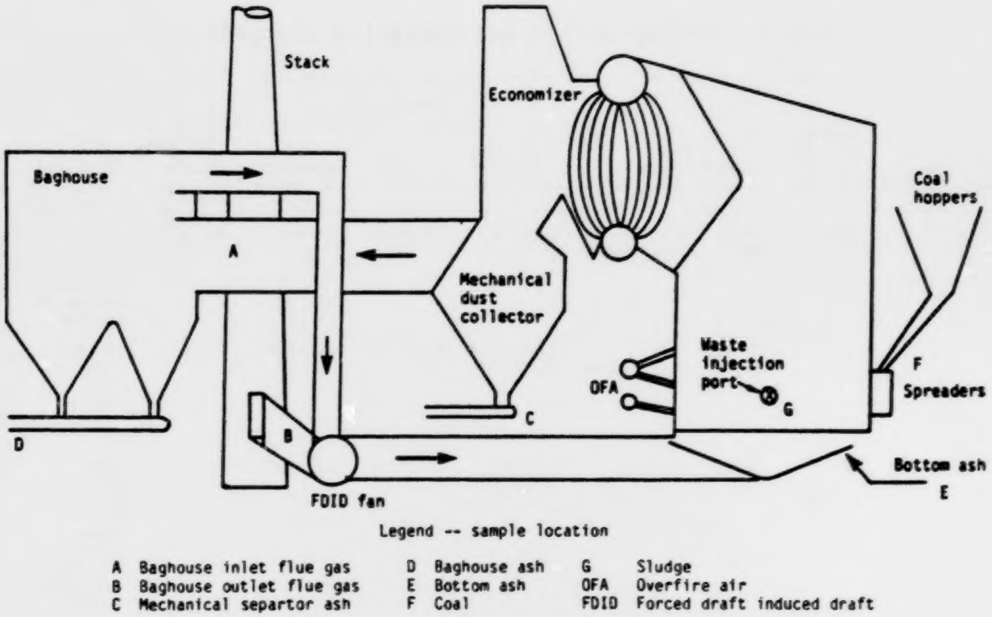

Stack
Economizer
Baghouse
A
Coal hoppers
Mechanical dust collector
Waste injection port
OFA
F
Spreaders
G
C
D
B
Bottom ash
E
FDID fan
Legend -- sample location
A Baghouse inlet flue gas
B Baghouse outlet flue gas
C Mechanical separtor ash
D Baghouse ash
E Bottom ash
F Coal
G Sludge
OFA Overfire air
FDID Forced draft induced draft

Figure 1. Site N -- site layout (not to scale).

with distillate oil spiked with trichlorobenzene and trichloroethylene to determine the effect of waste heating value on POHC destruction efficiency.

At Sites M and N, POHC injection pumps were used to spike the waste streams. This allowed better control of POHC concentration in the waste and POHC feedrate to the boiler. The sampling and analysis protocol consisted of the following:

- Continuous flue gas monitoring for O_2, CO_2, CO, NO_x, SO_2, and total unburned hydrocarbons (TUHC)
- Particulate and semivolatile organic sampling using the EPA Modified Method 5 (MM5) train; post test semivolatile analyses by gas chromatography/mass spectrometry (GC/MS); priority pollutant metals for Site N by furnace atomic absorption (AA)
- Volatile organic sampling by minivolatile organic sampling trains (VOST) and VOST protocols; onsite GC/Hall for chlorinated organics by direct desorption of mini-VOST samples; offsite laboratory GC/MS for priority pollutant organics by direct desorption of VOST samples
- HCl sampling by Modified EPA Method 6 (MM6) train; analyses by titration
- Particulate size distribution and metals by Andersen impactor stages at inlet and outlet of Site N baghouse; analyses by furnace AA
- Grab sample of waste and primary fuels; GC/MS for POHC analyses, and ultimate analyses by ASTM methods
- Grab sample of ash streams at Site N; selected analyses for metals by AA, semivolatile

ganics by GC/MS, and leachates by extraction procedures (EP) toxicity protocols

The bulk of volatile organic sampling and analysis was done with a simplified mini-VOST protocol (2). A simple Tenax trap was used with the VOST train for a 10 liter (L) sample of stack gas. Immediately following the sampling, the traps were taken to an onsite GC/Hall and thermally desorbed. Trap QC preparation was also performed onsite.

Tables 2 and 3 summarize continuously monitored gas emissions recorded during off-design and transient test conditions at the three test sites. During off-design tests,

Table 2. Summary of criteria flue gas emissions during off-design operation.

			As measured dry basis		Corrected to 3% O_2 dry basis			
Site	Test conditions	No. of tests	O_2 (%)	CO_2 (%)	CO (ppm)	SO_2 (ppm)	NO_x (ppm)	TUHC (ppm)
L	Low air, load, waste	10	3.7	10.5	320		365	3
L	Atomization upsets	6	4.0	12.0	242		400	3
L	Inverted atomizer	3	4.7	11.7	156		390	1
M	Low air	11	3.5	11.3	1011		105	39
M	Low air, high POHC	7	3.8	11.1	1548		81	38
M	No atomization steam	2	3.4	10.9	460		107	6
M	Improper burner	1	6.5	9.5	432		119	21
M	High POHC	11	7.2	8.6	201		105	7
M	Low air, low load	6	5.0	9.3	332		64	49
N	Low load, high air, sludge	3	9.7	9.4	89	1881	450	6
N	Low load, low air, sludge	1	6.4	11.5		1876	297	4
N	Low load, sludge	1	8.7	10.5	37	1895	398	23
N	Low load, high air, oil	1	10.1	8.4	78	1675	428	12
N	Low load, oil	3	8.0	10.9	47	1491	331	11

Table 3. Summary of criteria flue gas emissions during transient operation.

			As measured dry basis		Corrected to 3% O_2 dry basis			
Site	Test conditions	No. of tests	O_2 (%)	CO_2 (%)	CO (ppm)	SO_2 (ppm)	NO_x (ppm)	TUHC (ppm)
L	O_2 transients	1	3.3	10.7	156		330	1
L	Waste flow transients	5	4.3	11.0	271		401	1
L	Load transients	5	4.1	11.1	700		367	4
L	Soot blowing	4	4.6	11.5	195		387	2
M	Waste oil lightoff	5	6.3	9.2	412		105	23
M	Soot blowing	8	5.7	10.1	64		127	5
M	Unsteady oil flow	4	5.3	7.7	45		102	7

the boiler operational settings were selected to deliberately induce smoking or higher CO and TUHC emissions. For Site N, foreseen problems in clinkering of coal ash on the grate and baghouse blinding limited the degree of off-design and transient boiler operation investigated.

RESULTS

Tables 4 and 5 summarize the DREs measured during off-design and transient operation, respectively. Average DREs are calculated using the arithmetic averaging of individual test DREs. Tests are grouped according to specific boiler operating conditions investigated (e.g., low excess air, low steam load, etc.). A total chlorinated organic DRE is also reported. This value is based on the total amount of volatile chlorinated organics detected in the flue gas and the total amount of chlorinated organics (POHCs) burned with the waste. Thus, this value is always lower than the individual POHC DRE because it takes into consideration the levels of volatile chlorinated PICs also emitted during cofiring. It should also be clearly noted that these DRE values are based on volatile organics only and that emissions of semivolatiles were not included in the DRE equation.

Typically all individual POHCs were destroyed at greater than 99.99 percent efficiency regardless of the nonsteady state operating conditions of the boiler. Thus, despite the nonideal combustion conditions present in these boilers the thermal environment was such that POHC decomposition was not significantly affected. One noted exception is given for CCl_4 during low air at low steam load for the Site L boiler. Statistically, this simple measurement represents an anomaly in the data set since duplicate tests did not confirm this trend.

The total Cl DREs were also generally higher than 99.99 percent. Exceptions were recorded only for selected off-design (low air) and transient (sootblowing) tests. These results are an indication that volatile chlorinated PIC emissions were measured at orders of magnitude higher than unburned POHCs. During these tests, nonchlorinated volatile organic emissions were also increased. Sootblowing test results are of significance because it is hypothesized that soot generated during improper boiler operation may act as an absorbent for volatile PICs and POHCs, trapping these emissions on boiler internals until released during sootblowing.

The destructibility index (TCB>MCB >CCl_4>TCE) found during the steady-state tests and reported in laboratory-scale experiments (3), was not found for off-design operation. In fact, there does not appear to be any correlation between the measured DREs and the predicted ease of destruction for these compounds.

Figure 2 shows total chlorinated organics DRE versus CO for all three sites. High CO values are from nonsteady-state test conditions. The lack of a meaningful correlation is obvious. Note that, although there are several values less than 99.99 percent, the weighted average DRE for a given test condition is still greater than 99.99 percent. Also note that the nonsteady values (off-design and transient) are about the same as the steady-state values (normal). An attempt was made to fit a least square line to these data, but the correlation was poor and the correlation had only a slightly negative slope at an average value (intercept) of about 99.997 percent. In general, other attempts to correlate DRE with criteria gas emissions did not reveal any meaningful trends indicating that at this high level of

Table 4. Summary of average DREs for off-design operation.

Site	Description	No. of tests	Average Cl feed (mg/MJ)	Average DREs				
				Total Cl	CCl_4	MCB	TCE	TCB
L	Low air, load	10	227	99.9734 (99.9944)	99.9700 (99.9962)	99.9976 (<-excludes one low point)		
L	Atomization upsets	6	320	99.9921	99.9994	99.9956		
L	Inverted atomizer	3	413	99.9940	99.9988	99.9998		
M	Low air	11	204	99.9871	99.9996	99.9984		99.9997
M	Low air, high POHC	7	391	99.9963	99.9994	99.9993		99.9977
M	No atomization steam	2	179	99.9978		99.9987		
M	Improper burner	1	444	99.9990	99.9997	99.9994		
M	High POHC	11	368	99.9984	99.9993	99.9996		99.9989
M	Low air, low load	6		99.9927	99.9985	99.9973		
N	Low load, high air, sludge	8	692	99.9970			99.9997	99.9996
N	Low load, low air, sludge	3	510	99.9998			100	
N	Low load, sludge	3	489	99.9973			99.9999	
N	Low load, high air, oil	3	374	99.9989				99.9997
N	Low load, oil	6	441	99.9970			100	99.9995

MCB -- monochlorobenzene
TCE -- 1,1,2-trichloroethylene
TCB -- 1,2,4-trichlorobenzene

Table 5. Summary of average DREs for transient operation.

Site	Description	No. of tests	Average Cl feed (mg/MJ)	Average DREs				
				Total Cl	CCl_4	MCB	TCE	TCB
L	O_2 transients	1	92	99.9964	100.0000	99.9939		
L	Waste flow transients	5	324	99.9937	99.9948	99.9961		
L	Load transients	5	261	99.9974	99.9988	99.9995		
L	Soot blowing	4	302	99.9928	99.9991	99.9935		
M	Waste oil lightoff	5	377	99.9985	99.9993	99.9994		
M	Soot blowing	8	248	99.9782	99.9999	99.9968		99.9994
M	Unsteady oil flow	4	521	99.9960				99.9996

MCB -- Monochlorobenzene
TCE -- 1,1,2-trichloroethylene
TCB -- 1,2,4-trichlorobenzene

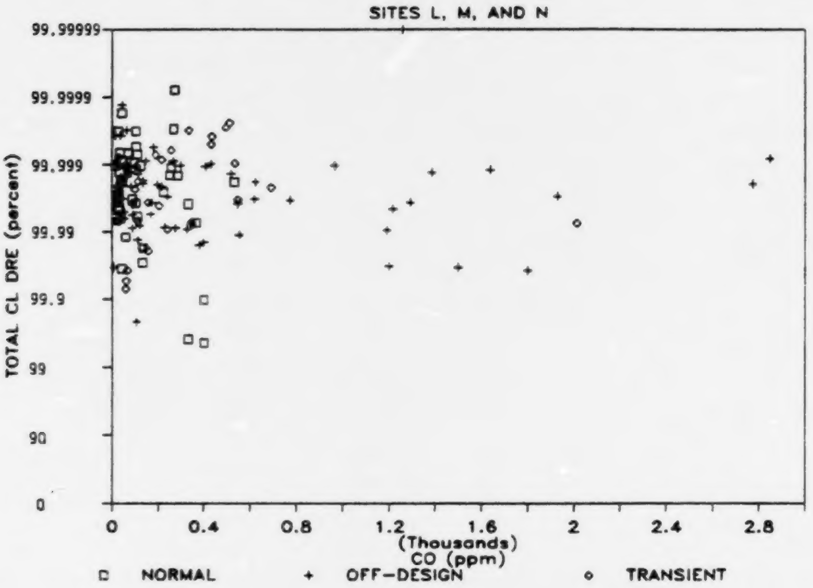


Figure 2. Total Cl DRE versus CO.

destruction, the DRE is essentially independent of other gaseous emissions such as CO and TUHC.

Figure 3 shows the CCl_4 DRE versus the boiler surface heat release rate. These plots gave the best correlation, though the correlation is not strong; the coefficient of fit is 0.19 (a value of 1.0 is a perfect fit). The least squares fit of a straight line correlation, shown on the graph, shows a small tendency for the DRE correlation to increase as the heat release rate increases. Again, the values for nonsteady-state operation are not significantly different than for normal operation. Generally, values for total PIC and POHC emissions tend to be higher for nonsteady-state operation, but this is not significantly reflected in the DREs.

ACKNOWLEDGEMENT

This research effort was sponsored by the Environmental Protection Agency under Contract 68-03-3241. Ivars Licis and Bob Mournighan of the Hazardous Waste Engineering Research Laboratory, and Marc Turgeon of the Office of Solid Waste and Emergency Response were the Project Officers. Their support and assistance during all phases of this effort was greatly appreciated. The authors also wish to acknowledge the contribution and logistical support from the management and technical personnel at each host site.

REFERENCES

1. Castaldini, C., et al., "Engineering Assessment Report, Hazardous Waste Cofiring in Industrial Boilers," Acurex Report TR-84-159/EE to USEPA under Contract No. 68-02-3188, June 1984.

2. Spannagel, U., et al., "Mini-VOST Field Analytical Protocol," Acurex Draft Report FR-85-159/EED

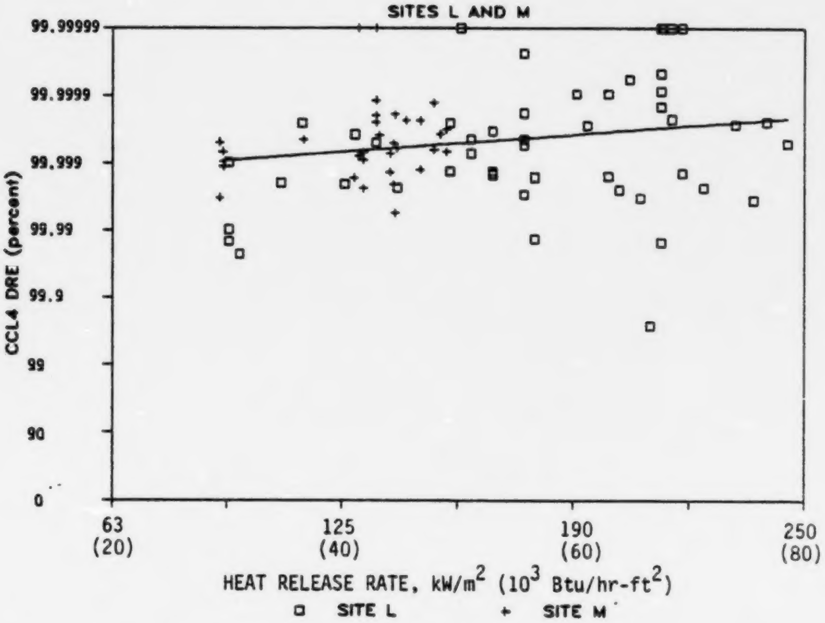


Figure 3. CCl_4 DRE versus the heat release rate.

to the USEPA under Contract 68-03-3241, July 1985.

3. Dellinger, B., et al., "Determination of Thermal Decomposition Properties of 20 Selected Hazardous Organic Compounds," Proceeding of the Tenth Annual Research Symposium, Incineration and Treatment of Hazardous Waste, EPA-600/9-84-022, September 1984.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

WASTE DESTRUCTION BY PLASMA ARC PYROLYSIS

Michael F. Joseph
Westinghouse Plasma Systems Canada Inc.
Niagara Falls, Ontario, Canada L2H 1J6

Thomas G. Barton
Pyrolysis Systems Incorporated
Kingston, Ontario, Canada K7K 6C2

ABSTRACT

A completely mobile system for the destruction of hazardous or highly toxic liquid organic wastes has completed initial testing in Canada and is now being marketed by Westinghouse Plasma Systems Incorporated of Westinghouse Electric Corporation. This technology has been under developement for the past 10 years and gives extremely high destruction efficiencies and low emissions for typically hard to destroy toxic wastes.

The Pyroplasma unit with a throughput rate of 3 gallons per minute (GPM), is contained in a single 48 foot tractor trailer and requires power, water and sanitary sewer to become completely operational. Mobilization requires only one to two days. The heart of the technology lies within the plasma torch, an electrical device which efficiently converts electrical energies to thermal energies in the form of a heated gas with temperatures in the 5-20,000 degree Celcius range. The entire system is computer controlled with numerous environmental, safety and operational failsafes as well as continuous process gas analysis.

In 1982 the developer of the Pyroplasma technology, Pyrolysis Systems Incorporated of Canada, entered into a contract with the New York State Department of Environmental Conservation and the EPA to design, construct, test and operate the plasma arc unit for use at the Love Canal site in New York State. The first three phases of work; design, construction, and testing, are now complete. The testing phase consisted of numerous hours of mechanical shakedown of the system with non-toxic solvents followed by extensive testing using carbon tetrachloride and PCBs. Destruction efficiencies ranging from 6 to 9 'nines' combined with low emissions of products of incomplete combustion make this technology environmentally and commercially attractive.

Preceding page blank

INTRODUCTION

In the past two decades it has become obvious that the large volumes and many types of hazardous industrial wastes produced pose a serious threat to both the public and the environment. It is estimated that over 290-300 million metric tons of hazardous and/or toxic wastes are generated on an annual basis (1,2) translating into an estimated greater than 10 billion dollar a year market. In 1976, the United States Environmental Protection Agency (EPA) responded to this threat with the enactment of the Resource Conservation and Recovery Act (RCRA) and the Toxic Substances Control Act (TSCA). This brought about a rapid increase into research for methods to destroy organic liquid and solid wastes. This was accelerated again in 1984 by the passing of the Hazardous and Solid Waste Amendments (HSWA) to RCRA which requires a series of landfill restrictions on eventually all hazardous wastes by 1990. The implementation of these amendments are dependent upon the availability of successfully demonstrated alternative technologies to replace existing land disposal practices.

Destruction technologies are regulated by RCRA and TSCA which specify all the necessary criteria that must be demonstrated before any technology can be permitted. These regulations apply to the operation of the process, the efficiency of destruction for the waste stream in question and certain restrictions as to the quality of emissions that must be achieved and maintained.

Efficiencies are measured as a destruction and removal efficiency (DRE) and expressed in percent as calculated by the following formula:

$$\text{DRE} = \frac{\text{Waste In} - \text{Waste Out}}{\text{Waste In}} \times 100$$

The waste is measured by the mass feed rate of the Principal Organic Hazardous Constituent (POHC). Under RCRA, hazardous waste facilities must maintain at least a 99.99% removal efficiency (99.9999% for dioxins) while technologies processing PCBs which are considered toxic and regulated under TSCA must operate at DREs greater than 99.9999%. There are also particulate and HCl emission restrictions. Also important are the Products of Incomplete Combustion (PICs) associated with the process. These are compounds which are not present in the actual feed stream but may be produced as a byproduct of the destruction itself such as highly toxic chlorinated dioxins and furans.

PURPOSE

While incineration is still recognized as one of the best demonstrated available technologies (BDAT) there has been a rapid increase in the number of innovative chemical and thermal processes for the ultimate destruction or reduction of hazardous wastes.

The development of the Pyroplasma^{T} technology was dependent upon several factors directly related to required operational criteria. In order to easily achieve destruction and removal efficiencies greater than the six 9's necessary for the most toxic of wastes an alternate source of thermal energy other than combustion was a prime consideration. The technology had to be competitive economically and of an appropriate commercial scale. The technology was also designed to be as mobile as possible so that the perception problems asociated with the 'not in my back yard' syndrome (NIMBY) could be alleviated.

APPROACH

A thermal plasma, properly applied to toxic waste destruction, provides a pyrolytic or reducing environment with several distinct advantages over conventional combustion technologies (3). The extremely high plasma temperatures combined with the flaring of the product gas assures high DREs. The reducing atmosphere reduces the production of oxygen containing PICs such as dioxins and furans. In addition, since the process is pyrolytic and large volumes of execess air are not required the scale of the equipment is small and can be easily made mobile while still allowing for throughput rates as high as 3 GPM, or about one ton per hour (see Figure 1).

Work on a pilot scale prototype over a five year period yielded preliminary results which indicated that the Pyroplasma technology could indeed be a viable thermal destruction technique. In 1982, Pyrolysis Systems Incorporated (PSI) of Canada signed a co-operative agreement with the New York State Department of Environmental Conservation (NYSDEC) providing funding for the design, construction, testing and operation at Love Canal of a one gallon per minute commercial scale Pyroplasma unit. The first three phases of work are now complete and the last phase is awaiting the necessary permitting. In 1985, PSI signed a joint venture partnership with Westinghouse Electric Company forming Westinghouse Plasma Systems to commercialize this technology.

Process Description

The heart of the system is the plasma torch (see Figure 2). A co-linear electrode arrangement and about 750 kilowatts (kW) of power are used to create an electric arc in the presence of a medium of low pressure air. Electrical energy absorbed by the air molecules raises them to highly excited states. During relaxation these molecules release thermal energy producing a plasma. When a process gas such as air is passed through this thermal plasma the result is a hot gas with temperatures in the 5,000-20,000 degree C range. Waste fluids are injected directly into the tail of the plasma and the hot process gas. The extremely high temperatures associated with the plasma torch provide enough energy for completed atomization of the waste molecules thus providing very high DREs with relatively low energy requirements, typically less than one kilowatt-hour per kilogram of waste.

The atoms then react in a recombination chamber according to chemical kinetic equilibriums and the minimization of Gibb's free energy, to form non-toxic type gases. The product gas typically comprises about 50% hydrogen, 30% carbon monoxide, 15% nitrogen and the remainder lower hydrocarbons such as methane and ethylene. Acid gas (HCl) formed from the destruction of chlorinated wastes is neutralized by caustic soda (NaOH) in a wet scrubber to give a

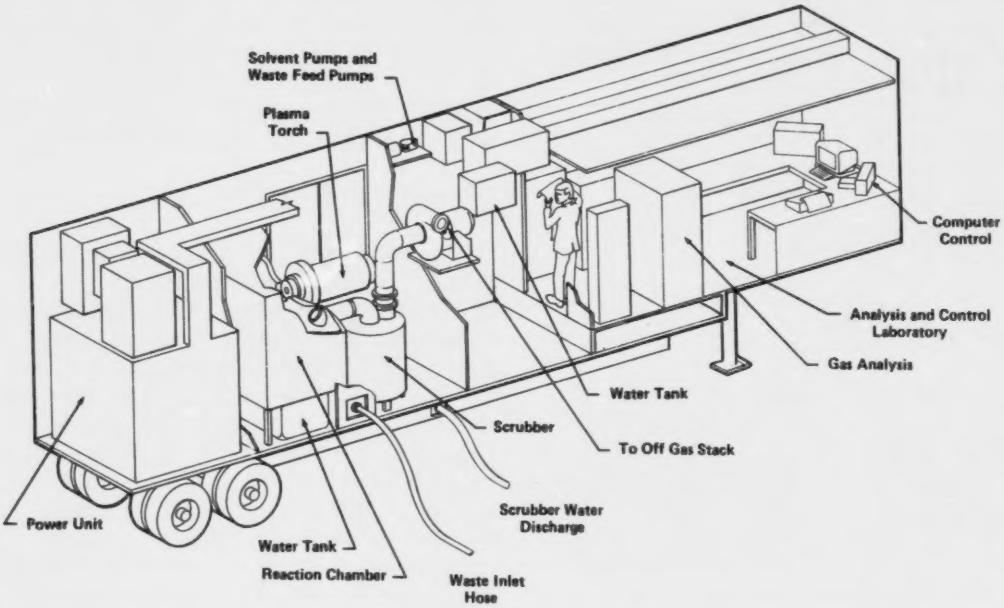

Solvent Pumps and Waste Feed Pumps
Plasma Torch
Computer Control
Analysis and Control Laboratory
Gas Analysis
Water Tank
Scrubber
To Off Gas Stack
Scrubber Water Discharge
Power Unit
Water Tank
Reaction Chamber
Waste Inlet Hose

Figure 1. Schematic of 3 GPM Mobile Plasma Arc Destruction Unit

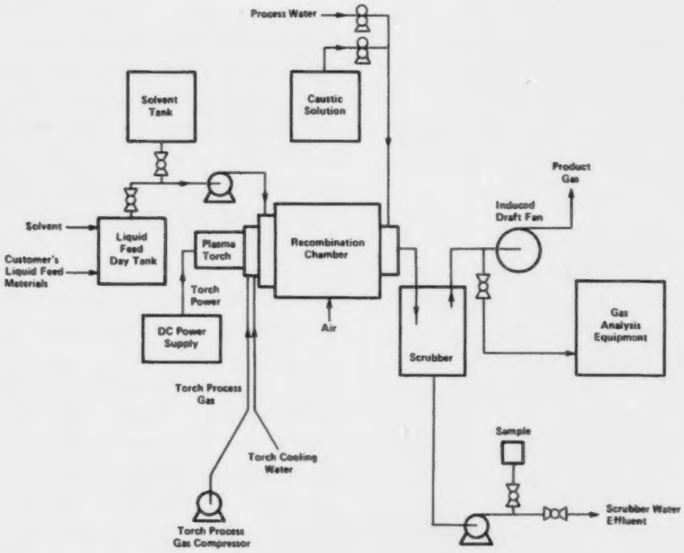

Process Water
Solvent Tank
Caustic Solution
Product Gas
Induced Draft Fan
Solvent
Customer's Liquid Feed Materials
Liquid Feed Day Tank
Plasma Torch
Recombination Chamber
Torch Power
DC Power Supply
Air
Scrubber
Gas Analysis Equipment
Torch Process Gas
Torch Cooling Water
Sample
Scrubber Water Effluent
Torch Process Gas Compressor

Figure 2. Mobile Pyroplasma Process Schematic

slightly salted (NaCl) scrubber effluent which is discharged along with any particulate carbon that may be formed. The product gas is drawn off the scrubber by an induction fan which maintains a negative system pressure and the gas is flared. Fuel values of the product gas are typically between 2-3 times the actual power required for the torch. The composition of the gas may be altered by careful blending of the waste feed prior to destruction or by the addition of other constituents such as water or air to the recombination chamber.

Operation begins with a non-toxic type solvent such as methanol and continues for about ten to fifteen minutes until the recombination chamber stabilizes at a predetermined temperature, typically about 1200-1400 C. A stable operating chamber temperature is an indication of balanced energy absorption of the torch power by the incoming wastes thus ensuring efficient waste destruction. Chamber temperature is controlled by adjustments in torch power, torch process gas flow or waste feed flow rate. Since the destruction process occurs in the plasma field, system destruction efficiencies do not depend upon the actual value of the reactor chamber temperature or residence times. The entire system is computer monitored through a series of temperature, pressure, flow and electrical sensors so that operational parameters and system efficiencies are maintained. There are a number of failsafes built into the system to minimize the risk to the environment even in the event of power failure, a worst case situation. Carbon monoxide, carbon dioxide, hydrogen, oxygen and total hydrocarbons of the bulk gas are measured on line for comparison to theoretical models.

Testing

The Pyroplasma process is capable of destroying a wide spectrum of liquid organic wastes. Materials were selected for testing purposes to demonstrate the ability of the plasma to process difficult to destroy, highly chlorinated wastes. In 1985 and early 1986, a rigorous series of tests were conducted with methyl ethyl ketone (MEK), ethanol (EtOH), methanol (MeOH), carbon tetrachloride (CCl_4) and transformer Askarel fluid (PCBs and trichlorobenzene). All tests were observed by both federal and state authorities from the United States, as well as federal, provincial and local Canadian authorities. All sampling and analyses were performed by external agencies as part of the New York State contract with PSI and the data has been reviewed and approved by the EPA.

RESULTS

Mechanical operation of the mobile plasma pyrolysis system was first verified by processing a non-chlorinated blend of MEK/MeOH (1:1 volume). Following this, three one-hour CCl_4 runs were conducted to demonstrate (i) the destruction efficiency with a hard to destroy chlorinated compound (ii) the stability of the system upon exposure to high concentrations of chlorine, and (iii) the effectiveness of the scrubber for HCl removal. The CCl_4 was blended with MEK/MeOH/H_2O and fed at a rate of one kilogram of CCl_4 per minute. DREs were greater than 99.99995% for all three runs based on measured residuals in all effluent streams. Stack emissions for CCl_4 were analytically non-detectable (see Table 1).

Following this stage of testing seven tests were performed using a blend of Askarel (Aroclors 1254/1260 in trichlorobenzene) in MEK/MeOH to determine the PCB destruction capability of the process. Three one-hour, one two-hour and three five-hour tests with feedstocks approximately 30-35% by mass Askarel gave DREs consistently greater than 99.99999% (see Table 2). Table 3 summarizes the HCl, particulate, NO_x, O_2, CO and CO_2 emissions for the flared product gas. Emissions of HCl, particulate and NO_x were below accepted Canadian and American regulatory agency guidelines.

In addition to the high destruction efficiencies, emissions of chlorinated dioxins and furans were usually below detection limits in both the gas and water effluents. For example, no chlorinated dioxins were detected in either the gas or water effluents in PCB test #9, the highest PCB concentration test. Typical of pyrolytic systems the products of incomplete combustions found were polyaromatic hydrocarbons (PAHs). Analytical data shows that better than 99.5% of the PAHs produced by the system were found to be absorbed on the particulate carbon in the water phase. Studies also show that when this carbon was removed from the scrubber water by simple filtration resultant PAH concentrations were in the low ppb range. PAH concentrations in the gas phase were below regulatory guideline limits.

These analytical results are even more meaningful if you consider the relatively low gas and water volumes associated with this pyrolytic process in combination with the emission concentrations expressed in mass per unit volume.

ACKNOWLEDGMENTS

The co-operation and assistance of the Environmental Protection Service and the Ministry of the Environment of Canada, and the Environmental Protection Agency and New York State Department of Environmental Conservation are much appreciated.

REFERENCES

1. Matey, J.S., and L.F. Tischler, 1986, 1984 Hazardous Waste Survey, Journal of the Air Pollution Control Assoc., vol. 36(6), pp.737-740.

2. Rich, L.A., 1986, Hazardous Waste Management, Chemical Week, August 20, pp.26-64.

3. Barton, T.G., 1984, Mobile Plasma Pyrolysis, Hazardous Waste, vol. 1(2), pp. 237-247.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Table 1. CCl_4 test results

Test (#)	Mass (%)	Input (kg/hr)	Output Air (mg/hr)	 Water (mg/hr)	 Total (mg/hr)	DE (%)
1	35.0	64.2	29.27*	2.51	31.78	99.99995
2	40.0	60.6	22.79*	9.85	32.64	99.99995
3	35.0	64.2	22.89*	6.26	29.15	99.99995

* number reported is analytical detection limit

Table 2. PCB test results

Test (#)	Mass (%)	Input (kg/hr)	Output Air (mg/hr)	 Water (mg/hr)	 Total (mg/hr)	DRE (%)
3	14.1	23.9	0.65*	4.08	4.73	99.999997
4	14.1	18.8	2.00	10.16	12.16	99.999994
5	11.5	19.8	6.96	18.76	25.72	99.99996
6	14.3	18.0	0.43*	0.41*	0.84	99.999998
7	12.5	17.5	0.02*	93.12	93.14	99.9999999
8	12.8	16.9	0.03*	19.56	19.59	99.9999999
9	17.5	26.7	0.33	0.75	1.08	99.999999

* number reported is analytical detection limit

Table 3. Flared product gas parameters@

Test (#)	O_2 (%)	CO (%)	CO_2 (%)	HCl (mg/M^3)	NO_x (ppm)	particulate (mg/M^3)
3	14.0	0.01	5.5	NA	117	10
4	14.5	0.01	5.0	43	NA	180
5	16.5	0.01	3.0	68	139	12.5
6	15.8	0.00	3.8	1.07	96	15.84
7	14.0	0.00	5.1	2.68	115	7.60
8	15.3	0.00	4.3	1.30	108	10.96
9	13.3	0.00	5.2	26.8	81	11.9

@ refers to PCB tests #3-#9 of Table 2

LEACHING CHARACTERISTICS OF RESIDUAL ASHES FROM THE INCINERATION OF MUNICIPAL SOLID WASTE

Tracey L. Clapp, David S. Kosson and Robert C. Ahlert
Rutgers University
Department of Chemical and Biochemical Engineering
Piscataway, New Jersey 08855

ABSTRACT

Preferred disposal methodology for municipal solid waste (MSW) has shifted to resource recovery processes, or incineration, from landfilling as land becomes scarce. However, management of residuals from incineration of MSW must be considered carefully. Leachability of flyash and bottom ash will be of increasing importance. Preliminary studies indicate that a substantial fraction of the ashes produced will not pass the RCRA extraction procedure (EP) and a greater fraction will not pass the proposed TCLP. Ashes failing these criteria will require disposal as hazardous wastes.

A laboratory investigation has been carried out to determine the leaching characteristics of flyash resulting from incineration of MSW from a mixed residential and commercial service area. Extractions under conditions similar to EP and with use of a mineral acid have been considered. Detailed equilibrium partitioning isotherms for RCRA regulated heavy metals have been developed. Results indicate that the total ionic strength of the resulting extract has significant influence on partitioning of some metals. In addition, under certain conditions, only a small fraction of the total metal content of the ash is readily leachable. Thus, the structure of the ash has considerable influence on leaching results.

INTRODUCTION

Land disposal of municipal solid wastes (MSW) in landfills has been increasing in recent years. Current estimates indicate that 144 million tons per year (as generated, with moisture) of municipal wastes are disposed of in this fashion and it is predicted that approximately 197 million tons of municipal solid wastes will be generated in 1990 [1]. Under present solid waste management practices, wastes are primarily disposed of in approved sanitary landfills. In addition to overflow, there are the problems of leachate generation by the infiltration of rainwater and methane gas production due to decomposition. At present, federal, state and local governmental agencies are seeking alternative methods for the safe disposal of solid wastes.

Thermal destruction, i.e., incineration with or without energy or substance recovery, is a means of solid waste management of increasing importance. Incineration is also a preferred means for disposal of many industrial and hazardous wastes. This method of treatment destroys solid waste through oxidation, i.e., exposure of the

Preceding page blank

solid material to high temperatures in the presence of air. The process results in the production of exhaust gases, solid residuals and contaminated quench and scrubbing waters. Ideally, the quality of these output streams should be such that free discharge of the gases, straight-forward wastewater treatment and conventional landfilling of the solid residuals are possible.

Inorganic species, including metals, metallic salts and oxides, SO_2, NO_x and HCl, pass through combustion or are formed and appear in various free and combined states in all incinerator residuals. There are two types of solid residuals from incineration. Flyash is the gasborne particulate residue collected from incinerator flue gases using state-of-the-art air pollution control devices, e.g., venturi scrubbers and baghouses or electrostatic precipitators. Bottom ash is the heavier preliminary ash residual collected from the primary combustor, quench water and scrub water. Because of the sorption characteristics of ash, and flyash in particular, as well as the volatilization/condensation properties of metals, the process of incineration tends to condense metal and metal oxides onto and within the ash particles. To predict environmental impacts and to avoid leaching of contaminants into the environment, a complete understanding of the composition and chemical behavior of flyash is essential. Leaching of contaminants from landfilled ash is one of the pathways by which toxic substances can migrate to groundwater.

To simulate the mobility of inorganic constituents from wastes after landfilling, the U.S. Environmental Protection Agency established a laboratory batch leaching test known as the Extraction Procedure (EP). The EP was promulgated under the authority of the Resource Conservation and Recovery Act of 1976 [2]. This procedure employs the use of a dilute solution of acetic acid (HOAc) as the leaching medium. This volatile fatty acid is common in leachate from municipal waste, since it is a byproduct of the first stage of anerobic degradation. However, there has been much recent criticism of the applicability of the EP. As a result of the criticisms, a new test was developed and proposed [3]. The Toxicity Characteristic Leaching Procedure (TCLP) differs from the EP in that the extractant is either buffered acetic acid or dilute acetic acid depending on the initial pH of slurried solid. The extractant is introduced in one addition and the pH is no longer maintained externally. The extraction is run for 18 hours in a closed extraction vessel. Both EP and TCLP methodologies have been used to evaluate incinerator ash behavior after landfilling.

PURPOSE

The focus of this paper is to examine the behavior of metals found in residual flyash from the combustion of MSW. Initial research began with experiments simulating the EP and TCLP procedures [4]. In addition, total metal content of the ash was determined through sequential acid digestions using nitric and perchloric acid. Research was then initiated to examine more thoroughly the leach potential of certain metals since both the EP and TCLP impose severe constraints upon leach conditions. Equilibrium isotherms were established at a series of pH's by varying the extractant-to-solid ratio and a variety of metals were examined. Acetic and hydrochloric acids (HCl) extractants were examined, and equilibrium partitioning isotherms were developed. This information can be used to provide a more thorough understanding of the metal chemistry of solid residuals. Such an understanding is essential in order to develop on-line process equipment for the systematic removal or recovery of these metals.

APPROACH

Figure 1 is a graphic representation of the incinerator used to generate the ash assayed in this study. The MSW is fed into a partially rotating primary combustor, followed by the secondary, fixed after-burner. Solid residuals from the primary solids combustor, quench tower and venturi scrubber all feed into an ashpit. Bottom ash is sampled from the ashpit and flyash is collected from three baghouses.

Samples of ash were collected from a demonstration burn of MSW generated from a residential community in New Jersey. Two flyash grab samples were taken at the conclusion of the burn. The samples were combined and mixed well to minimize the effect of heterogenity of the bulk composite.

Concentrations of lead, cadmium, copper, chromium, zinc, aluminum, nickel and silver were determined by Atomic Absorption Spectroscopy (AAS). Dissolutions for total metal determinations were carried out in replicate using 1:1 nitric acid/perchloric acid sequential digestions. Two grams of ash were placed in the bottom of a 100 ml Kjeldahl flask. Twenty ml. of concentrated nitric acid were slowly added along with a few teflon boiling chips. The mixture was allowed to boil slowly for two hours. After cooling, 20 ml of 70 v/o perchloric acid were introduced and the mixture was reboiled for an additional two hours using a trap to catch any escaping perchloric acid fumes. The digested sample was filtered and diluted quantitatively to 100 ml.

Ten gram samples (in replicate) of the flyash were used in EP and TCLP extraction experiments. Experiments were carried out with a methodology comparable to the Extraction Procedure Toxicity Characteristic. The solid material was weighed and placed in a beaker with deionized water, at a liquid-to-solid ratio of 16:1. An overhead stirrer equipped with a teflon stirring rod was used to provide sufficient agitation to the mixture. The pH of the solution was monitored during the course of the extraction; pH was maintained at 5.0 +/- 0.2 with 0.5N acetic acid addition, not exceeding 4 ml of acid per gram of ash. At the end of twenty-four hours, deionized water was added to bring the final mix to a 20:1 extractant-to-solid ratio.

Experiments designed to simulate the TCLP were carried out using ten grams of ash and 200 ml of extraction fluid. This solution was prepared by diluting 5.7 ml glacial HOAc to 500 ml with ASTM Type 2 water, adding 64.3 ml of 1.0 N NaOH, and diluting to a volume of 1 liter. After eighteen hours of agitation (using the same apparatus as in EP methodology), samples were filtered and analyzed.

Elemental analysis was done with a Perkin Elmer 3030 Atomic Absorption Spectrophotometer (AA). All metals with the exception of aluminum were detected using an air-acetylene flame; aluminum detection required the use of a nitrous oxide-actylene flame.

To examine leaching potential, various extraction liquids were employed; pure deionized H_2O (pH 7), dilute aqueous HOAc (pH 3, 5), and dilute aqueous HCl (pH 1,2,3,5). Equilibrium isotherms were constructed at each of these pH's by variation of the extractant-to-solid ratio. A fractional factorial experimental design, with replication, was employed (Table 1). Five gram samples of the flyash were used in each extraction experiment.

Equilibration time was established through a series of experiments extending over a period of five days. Equilibration was based upon a liquid-to-solid ratio of 20 to 1 and a neutral pH since these two conditions were the mildest and would be expected to reach equilibrium most slowly.

RESULTS

Data for total metal concentrations as well as EP and TCLP results for these ashes are presented in Table 2. The concentrations of cadmium and lead leached from the flyash were found to exceed EP and TCLP regulatory limits. Other metals, such as nickel, chromium, and silver were extracted in low concentrations. The amount of several of the metals extracted by EP or TCLP represents only a small fraction of the total quantity of the metal extractable.

The time required to attain extraction equilibrium is presented in Figures 2 and 3. Equilibrium was approached at 24 hours for every metal tested. Therefore, all subsequent extractions were carried out with a 24 hour contacting period.

Extraction of lead at a pH of 3 for acetic acid, and a pH of 1 for HCl was substantial. Figures 4 and 5 display the final pH after 24 hours. At initial extractant pHs of 7 and 5 for acetic acid and 7, 5, and 3 for hydrochloric, the buffering capacity of the ash was demonstrated. Final extraction pHs were all approximately 6. At a pH of 3 for acetic acid and 2 and 1 for hydrochloric, the buffering capacity of the ash was finally overcome. At this point, lead extraction was substantial, clearly indicating a strong pH dependency. In addition, it can be seen that at a 40 to 1 liquid-to-solid ratio, lead extraction still did not reach a maximum quantity. Expansion of the acetic acid pH 3 extraction curve to a liquid to solid ratio of 100 to 1 shows that the maximum was finally reached.

Lead behavior as shown in figures 6 and 7 was dramatically affected by both pH and liquid-to-solid ratio. At pH's of 5 and 7, as the liquid to solid ratio increased, the equilibrium aqueous phase lead content decreased. One possible explanation for this behavior is that at low liquid-to-solid ratios, the solution chemistry (salting in/out effects) controlled lead extraction. This hypothesis is further supported by the fact that at a 1:1 liquid-to-solid ratio extractant solutions at an initial pH of 7, 5, and 3 removed approximately the same quantity of lead. At a pH of 1, it would be plausible that at low liquid-to-solid ratios, solution chemistry controlled pH, but the highly acidic conditions also played a substantial part in extraction.

Equilibrium isotherms for the different extractants and extractant pHs examined are presented in Figures 8 and 9. These isotherms describe the partitioning of lead between the solid and aqueous phases. Generally, a monotonically increasing response is expected. However, the response observed at pHs 7 (H_2O), 5 (HOAc) and 5 and 3 (HCl) deviate from this pattern. This is most likely the result of the confounding effects of equilibrium pH, aqueous phase solubility (salting in/out, i.e., aqueous phase ionic strength), extractant efficiency and lead species present.

Cadmium and lead present in the flyash from MSW incineration pose a serious disposal problem. The quantities of these metals available for extraction are high and not necessarily accurately reflected by EP or TCLP measurements. EP and TCLP methodology dictate a 20 to 1 liquid-to-solid ratio and a relatively high pH. From Figures 6 and 7, it is clear that these extraction parameters dictate a removal of only a small fraction of the available lead.

CONCLUSIONS

Lead extraction is dramatically affected by pH, liquid-to-solid ratio, and extractant type. The precise nature of these affectations remains to be explored. Chemical behavior must be examined in detail in the regions where solution chemistry controls extraction.

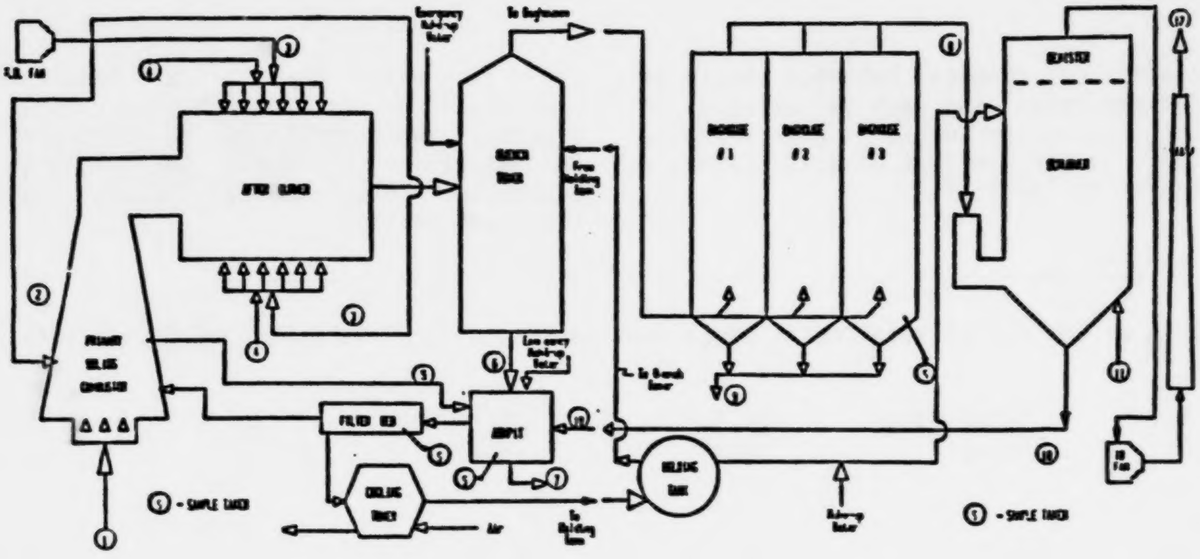

AFTER BURNER
QUENCH TOWER
BAGHOUSE #1
BAGHOUSE #2
BAGHOUSE #3
DEMISTER
SCRUBBER
HOLDING TANK
COOLING TOWER
Air
ID Fan
Ⓢ - SAMPLE TAKEN
Ⓢ - SAMPLE TAKEN

FIGURE 1: Process Flow Diagram of the Incinerator Sampled for this Study.

TABLE 1

EXPERIMENTAL DESIGN - Extractants Used at Different Liquid to Solid Ratios and pHs.

LIQUID TO SOLID RATIO (ml Extractant/g Ash)

pH (Acid Strength)	.5	1	2	4	6	8	10	12	14	16	18	20	50	100
1			HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl		HCl		
2			HCl	HCl		HCl	HCl	HCl	HCl	HCl		HCl	HCl	
3	HOAc	HOAc	HCl HOAc	HCl HOAc	HCl HOAc	HCl HOAc	HCl HOAc	HCl HOAc	HCl	HCl HOAc		HCl HOAc	HCl HOAc	HOAc
4														
5	HOAc		HOAc	HCl HOAc	HCl HOAc	HCl	HCl HOAc	HCl HOAc	HCl HOAc	HCl HOAc		HCl HOAc	HCl HOAc	
6														
7	H_2O		H_2O	H_2O	H_2O		H_2O	H_2O	H_2O	H_2O		H_2O	H_2O	

NOTE: Each test case was carried out in duplicate.
118 extractions were carried out.

In addition, chemical behavior should be examined when the ash is exposed to other extractant media. For example, H_2SO_4 is another type of acid commonly present in landfills.

It is only through a complete understanding of this behavior that processes and controls can be developed to stabilize residuals to minimize subsequent environmental impact and treatment costs.

Table 2. Results of total metal digestion and EP and TCLP extraction of flyash samples.

Metal	Total Metal (ppm)	EP Tox. (ppm)	TCLP (ppm)	Limits	
				EP	TCLP (ppm)
Cu	605	9	15	-	-
Cr	35	<1	<1	5.0	(5.0)
Ni	20	<1	<1	-	-
Cd	597	25	24	1.0	(1.0)
Pb	4271	2	9	5.0	(0.2)
Ag	43	2	2	5.0	(5.0)
Zn	19533	-	-	-	-
Al	1923	-	-	-	-

ACKNOWLEDGEMENTS

The authors would like to thank Miss Peggi Abrahamson, Miss Ruth Ann Geddings and Mr. Stephen White for their dedication and conscientious laboratory work. This research was funded by the New Jersey Institute for Hazardous and Toxic Waste Management.

REFERENCES

1. Schomaker, Norbert B., "Current Research on Land Disposal of Municipal Solid Wastes", Municipal Solid Waste: Land Disposal, Proceedings of the Fifth Annual Research Symposium, Orlando, Florida, pp. 9 - 31, (March 1979).

2. The Federal Register, Vol. 45(98), Pps. 33127 - 33129, (19 May 1980).

3. The Federal Register, Volume 51(9), Pps. 1750 - 1758, (14 January 1986).

4. Clapp, T.L., Magee, J.F. II, Ahlert, R.C., and Kosson, D.S., "Municipal Solid Waste Composition and the Behavior of Metals in Incinerator Ashes", Environmental Progress, In Press.

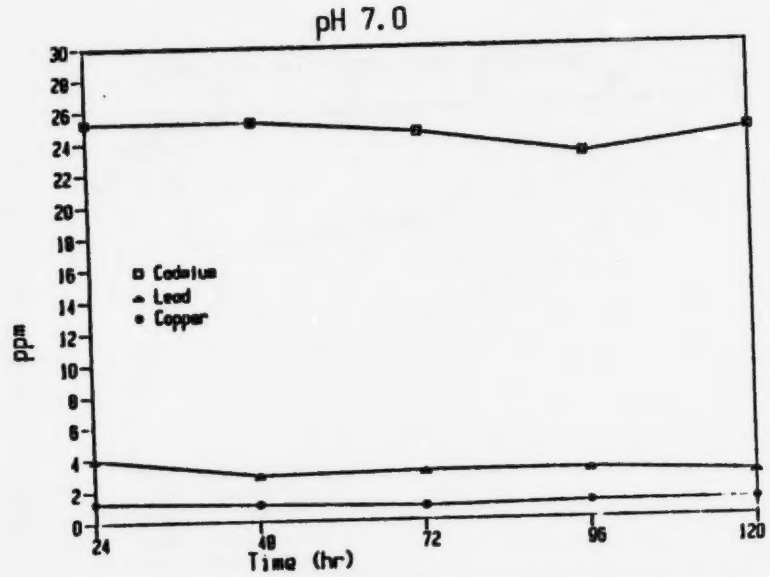


FIGURE 2

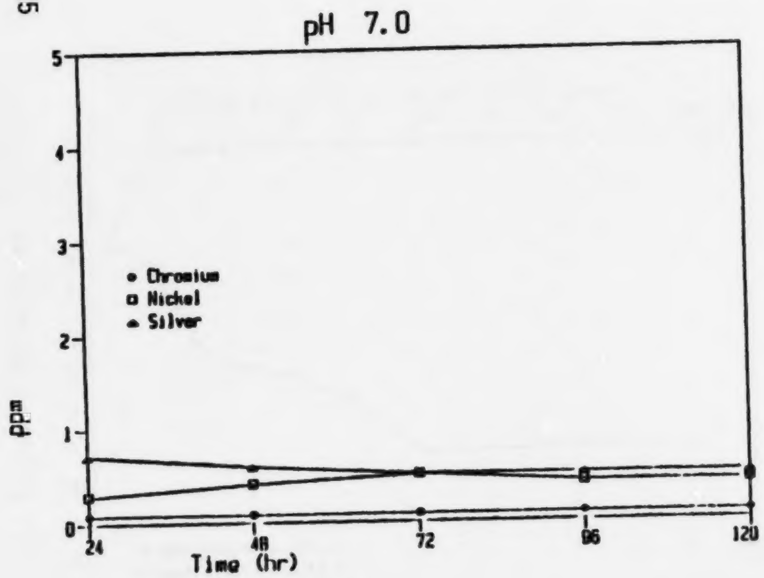


FIGURE 3

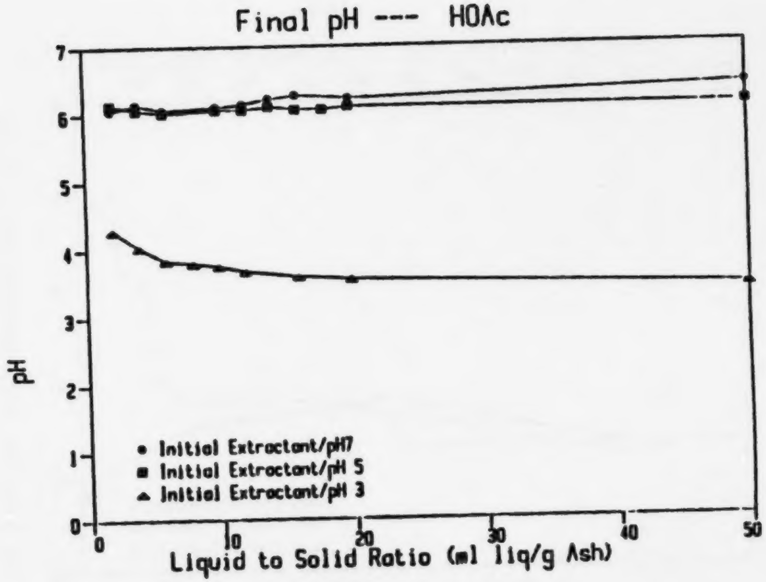


FIGURE 4

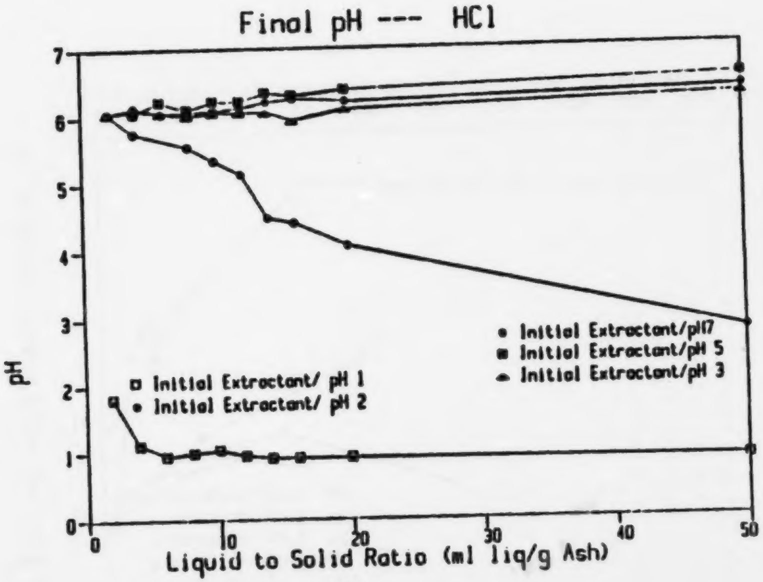


FIGURE 5

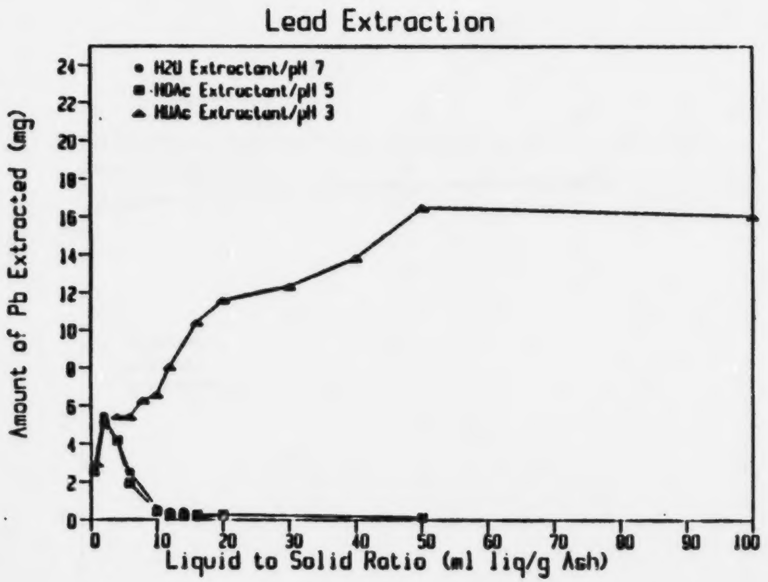


FIGURE 6

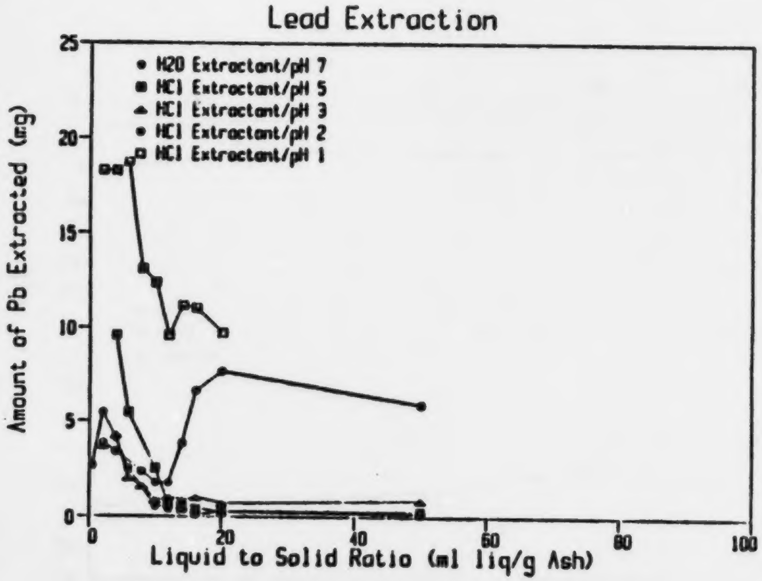


FIGURE 7

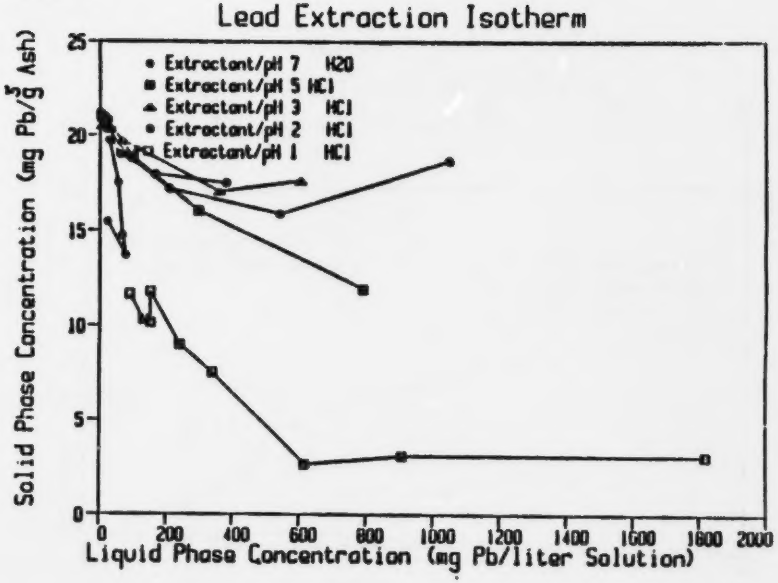


FIGURE 8

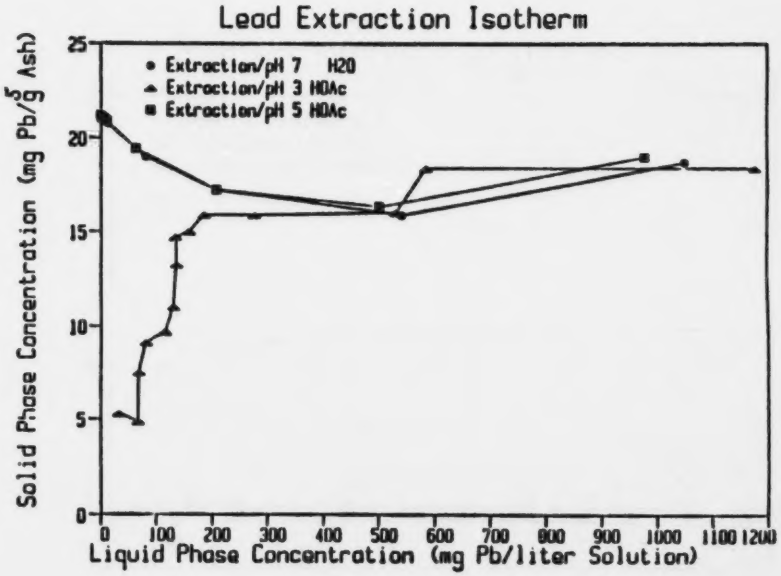


FIGURE 9

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

THE CLEAN-UP OF CONTAMINATED SOIL BY THERMAL DESORPTION

JoAnn S. Lighty, David W. Pershing
Chemical Engineering Department
3062 Merrill Engineering Building
University of Utah
Salt Lake City, Utah 84112

Vic A. Cundy, Frank R. Groves, Jr.
Departments of Mechanical and Chemical Engineering
Louisiana State University
Baton Rouge, Louisiana 70803

David G. Linz
Environment and Safety Research
Gas Research Institute
Chicago, Illinois 60631

ABSTRACT

The overall goal of this research is to develop an understanding of the fundamental transport phenomena associated with the evolution of hazardous materials from solids, in particular contaminated soils. At the present time, incineration is a relatively costly alternative for the clean-up of contaminated soils and it may render the soil inert. A more economical option is to desorb the contaminants from the soil at lower temperatures and then use high temperature incineration to decompose the hazardous off-gases. This work is aimed at providing fundamental rate information which may be used to model the thermal desorption of contaminants from soils under a wide variety of thermal conditions.

The experimental approach is three-fold. First, a bench-scale particle characterization reactor (PCR) has been developed and is being used to characterize intraparticle transport under conditions where the bulk concentration and temperature at the particle surface are known. Following these studies, a packed bed reactor will be used to examine interparticle transport within a well characterized bed of particles. In the third portion of the work, a 73,000 Watt pilot-scale rotary kiln will be used to obtain time resolved measurements of trace species evolution. This paper reports recent PCR and kiln results; it does not address the packed bed reactor studies since they are just being initiated. The PCR results indicate that soil pore structure is important in the desorption of contaminants from soil particles and that the desorption/diffusion step is probably a controlling mechanism.

Preceding page blank

INTRODUCTION

The identification of an increasing number of Superfund sites has brought into focus the issues concerning the proper disposal of hazardous industrial waste and remediation of contaminated soils. At the present time there are several commercially available treatment alternatives including redistribution where the hazardous material is loaded into barrels and redisposed in an approved land fill, (6) and thermal incineration where the hazardous material is destroyed by high temperature. Redistribution is becoming less feasible due to the onset of stringent federal and state permit requirements for land fills and this strategy only postpones the problem for future generations. Conversely, incineration is a proven technology and a permanent disposal strategy for most hazardous organic compounds (3) excluding heavy metals; however, incineration is costly due to initial capital investment and auxiliary fuel requirements and it results in a sterile soil.

At the present time the fundamentals of incineration are not well understood and the rate controlling steps have not been fully identified. Additional basic research is required before conventional thermal incineration can be fully optimized and auxiliary fuel minimized. In addition, it is possible that present incineration technology could be modified to include a lower temperature desorption step (1,2,4) followed by gas clean up (by chemical or thermal means). This concept would require less auxiliary fuel because the solid phase would not be exposed to extremely high temperature. The desorption process could be accomplished in various types of incineration or indirect fired equipment where there is good mixing between the contaminated soil and the desorbent gas, e.g. a rotary kiln, a rotary dryer, or a heat screw conveyer.

PURPOSE

The work reported in this paper focuses on establishing an understanding of the heat and mass transfer rates in the desorption of contaminants from a particle of soil where the bulk stream temperature and concentration at the particle surface are known. Using this information, the intrinsic desorption rates can be characterized and a model developed. In addition, preliminary kiln studies have been completed to demonstrate the utility of this information.

Future research in this area will examine the heat and mass transfer mechanisms controlling the evolution rate in a packed bed reactor, where temperature and concentration gradients exist within the bed. By combining the rate information from both the intraparticle and interparticle experiments, with the data from the rotary kiln simulator, it will be possible to develop an overall kiln model which can be used to predict the evolution of contaminants from the bed, and hopefully optimize and predict performance.

APPROACH

The overall approach in this program is based on the concept that the contaminated solid charge in a rotary kiln can be viewed as a bed containing many layers of large clumps that are being slowly stirred. The clumps are assumed to consist of an aggregate of smaller particles with varying size distributions and each of the particles may contain internal pore structure. Typical contaminants may exist: 1) absorbed onto the internal pore structure of the particles, 2) absorbed onto the external surface of the particles within clump, or 3) as separate crystals within the clump. Figure 1 shows a schematic of a typical contaminated soil particle and indicates that the particle aggregate may also contain significant water.

The experimental testing has been designed to characterize each phase of the decontamination process. In particular it will focus on 1) the evolution of hydrocarbons from within the pore structure of the soil and the subsequent diffusion to the particle surface, 2) the diffusion of contaminants through the voids of the clump structure to the clump surface, and 3) the diffusion of the contaminant species from the clump surface to the top of the bed.

A four task program has been developed. The initial task is focusing on the development of appropriate experimental methods for the preparation and characterization of hazardous wastes appropriate to the study. The subsequent three tasks are each designed to characterize and define the rate limiting step in the evolution of contaminant species from a typical contaminated particle, a typical aggregate of particles (clump), and the rotary kiln bed itself (layers of clumps) respectively. Three experimental reactor systems are being used in this study:

- °A particle characterization reactor to investigate intraparticle effects,
- °A controlled temperature packed bed reactor to characterize interparticle effects within an aggregate of particles, and
- °A pilot scale rotary kiln to characterize bed evolution and mixing.

This paper summarizes recently obtained results from the particle characterization reactor along with initial data from the rotary kiln.

EXPERIMENTAL FACILITIES

Particle Characterization Reactor

The bench scale particle characterization reactor (PCR), shown in Figure 2, was designed to minimize external heat and mass transfer resistances so that the boundary conditions at the particle edge were well characterized and did not vary as a function of time. Preliminary experimental studies have indicated that the PCR can be operated with essentially no temperature gradients within the solid bed.

The particle characterization reactor is composed of two concentric pyrex glass tubes of 7.6 and 15.2 cm diameter respectively held vertically between two stainless steel flanges. A bed of soil with a known contaminant concentration is loaded into the inner pyrex tube. The soil is contaminated by introducing contaminant into a bottle of soil, mixing the bottle, and letting the soil/contaminant mixture adsorb for 24 hours. Nitrogen gas passes through the annulus between the two tubes and down through the bed where the desorption occurs. The bed is supported on a wire mesh of nickel chromium gauze (24 gauge, 16 mesh) and polyester monofilament (200 mesh). Incoming gas, exit gas, and axial and radial soil temperatures are measured with thermocouples. The gas is heated using a 5.1 cm copper tube wrapped with a 600 watt electric heater and fiberglass insulation. The heater output is controlled using a variable voltage transformer.

Two 6.4 mm diameter nickel gas sample probes are located below the bed. The sample gas from both probes is combined external to the apparatus and analyzed using GC/FID techniques with a Porapak-P column. A 6 port valve is activated approximately every three minutes allowing a volume of sample to be analyzed.

Rotary Kiln

The pilot scale rotary kiln, shown in Figure 3, is constructed in three, refractory-lined steel sections. The core of the main reactor is 61 cm in inside diameter by 61 cm long and rotates at a speed of 0.5 to 2 rpm. The kiln burner fires axial and/or radial natural gas at a nominal rating of 73 kW. The kiln has been designed to simulate a full scale unit by replacing the variable of distance in a full scale system with that of time in the pilot scale. A batch of soil is loaded into the pilot scale kiln and burned for a predetermined residence time. By sampling the simulator's gas and solid phases as functions of time, it is possible to characterize the fate of a control volume of solid moving through a full scale rotary kiln (see Figure 4). The simulator's gas burner can be moved away from the soil bed as time proceeds to further simulate the movement of a control volume of solid away from the primary flame in a full scale kiln.

PRELIMINARY RESULTS

Particle Characterization Reactor

Initially the particle characterization reactor experiments focused on verifying the operation of the reactor at the baseline test conditions (5). Several soil bed depths and nitrogen flow rates were studied to establish the operating envelope for the reactor. Additional studies on the influence of bed stirring were also performed. In these experiments the soil bed was mixed with a stirrer operating at 45 RPM. These results indicated that a soil bed depth of 1.3 cm and a nitrogen flow rate of 5.7 l/m (the standard operating conditions) are well within the operating envelope of the PCR.

One of the primary variables affecting the rate of contaminant evolution is the type of soil. Figure 5 summarizes a series of experiments on the rate of 0.5 weight percent p-xylene evolution from various materials whose properties are shown in Table 1. The data of Figure 5 are reported as a normalized evolution rate, the rate of p-xylene evolved (gm/min) normalized with respect to the initial amount (gm) of p-xylene in the soil. With nonporous glass beads or sand, the evolution rate is initially very high and falls off rapidly. With more porous clay or peat, the rate declines quickly and then the decline slows. In addition, with the porous clay and peat the overall evolution was only approximately 80% over the period of the test, while the sand and glass beads exhibited a 99.99% p-xylene evolution. The initial evolution rate for all four materials was high due to surface evaporation as expected. The rate changes with time because of the change in the surface area covered by the p-xylene as evaporation proceeds. The nonporous glass beads and sand contained little internal surface area; hence, the rate of evolution decreases monotonically. The evolution data for the peat and clay particles suggest the existence of two, very different processes. The initial steep region is almost certainly associated with p-xylene evaporation from the external particle surface as with the glass beads and sand; however, the second region with almost constant evolution rate probably represents the desorption of p-xylene out of the pores of the soil particles. These results suggest that the internal pore structure of the soil particles is important in the desorption of contaminants and that intraparticle desorption/diffusion will likely be one of the rate controlling steps.

Evolution rate data were also obtained over a limited range of temperatures (25 to 140° C) as illustrated in Figure 6. Higher temperatures produced higher p-xylene evolution rates in both the evaporation and desorption/diffusion regimes as expected. The evaporation rate increases with temperature due to the increase in the partial pressure of p-xylene at higher temperatures. According to molecular theory, both the desorption and diffusion should also increase with increasing temperature, producing a evolution rate from the pores as well.

Rotary Kiln

Similar contaminant evolution rate data were obtained with 0.5 weight percent p-xylene on the sand particles using the rotary kiln simulator. Figure 7 summarizes typical kiln results obtained at 500° C; the results from an ambient temperature PCR run are shown for comparison purposes. As in the particle characterization experiments, the bulk of the contaminant is evolved very rapidly in the evaporation region; however, even at this significantly elevated temperature (500° C) the evolution of the final contaminant fraction is relatively slow and probably dominated by desorption/diffusion processes.

Hopefully these studies, coupled with the packed-bed reactor studies and the particle characterization research will help develop a full understanding of the rate mechanisms associated with the desorption and diffusion processes. While these experiments are focusing primarily on the rotary kiln environment, the fundamental results should be equally applicable to other types of solids handling equipment.

Future Work

Future studies will extend the experiments reported here to higher temperatures (up to 650°C) and will include consideration of other surrogate contaminants (e.g. gasoline, naphthalene, and coal tars) as well as actual field samples. The effects of moisture and particle size will also be examined. These experimental studies are being supported by coordinated mathematical modeling activities. Theoretical analysis is being used to decouple the desorption and diffusion steps and the data from this regime are being used to quantify the diffusivity and desorption equilibrium constants as functions of temperature, contaminant composition, and substrate composition. Two dimensional fluid mechanic and heat transfer models are being used to support the kiln simulation experiments.

ACKNOWLEDGMENTS

Funding from the Gas Research Institute, the National Science Foundation, and the NSF Advanced Combustion Engineering Research Center (ACERC) is appreciated, as well as the assistance of Mr. Ray Cayias of the Department of Chemical Engineering, University of Utah in the fabrication of the PCR.

REFERENCES

1. deLeer, Ed W. B., et al., "Thermal Cleaning of Soil Contaminated with Cyanide Wastes from Former Coal Gasification Plants," 1985, In: Proceedings, Conference on New Frontiers for Hazardous Waste Mangement, Pittsburgh, PA.

2. Dev, Harsh, 1986, "Radio Frequency Enhanced In-Situ Decontamination of Soils Contaminated with Halogenated Hydrocarbons," In: Proceedings, Twelfth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, Cincinnati, OH.

3. Freestone, F., et al., 1986, "Evaluation of On-Site Incineration for Cleanup of Dioxin-Contaminated Materials," In: Proceedings, Twelfth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, Cincinnati, OH.

4. Koltuniak, D. L., 1986, "In-Situ Air Stripping Cleans Contaminated Soil," Chemical Engineering, August 18, pp. 30-31.

5. Lighty, J. S., D. W. Pershing, and V. A. Cundy, "A Device to Characterize Phenomena During the Desorption of Contaminants from Soils," submitted to Review of Scientific Instruments, in press.

6. Singh, U.P., et al., 1984, "Cleanup of Miami Drum Hazardous Waste Site," Journal of Environmental Engineering, Vol. 110, pp. 343-355.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

HIGH TEMPERATURE SLAGGING INCINERATION OF HAZARDOUS WASTE

Rik Vanbrabant
Norbert Van de Voorde
SCK/CEN
Belgian Nuclear Research Center (SCK/CEN)
Waste Treatment Department
Mol, B-2400, Belgium

ABSTRACT

The SCK/CEN, as the treatment center for the low level radioactive waste in Belgium, develops appropriate treatment systems for different kinds of wastes. Since more than ten years, the technical concept of the high temperature slagging incineration system has been developed and improved. The construction of the first demonstration plant was initiated in 1974. Since then the system has been operated regularly and further developed with the view to industrial operations. Now it handles about 5 tons of waste in a week. The waste which is treated consists of low level beta/gamma and alpha-contaminated radioactive waste. Because of the special characteristics the system is thought to be an excellent incineration system for industrial hazardous waste as well. Recently the SCK/CEN has received the authorization to treat industrial hazardous waste in the same installation. Preliminary tests have been executed on special waste products, such as PCB-contaminated liquids, with excellent incineration results. Incineration efficiency up to 99,9999 % could be obtained.

The SCK/CEN decided to build a new facility for the treatment of this special kind of overlapping waste streams namely, potentially radioactive contaminated or low level contaminated waste, and highly toxic industrial hazardous waste. This plant is called HAWAI-system, which stands for HAzardous WAste Incineration system, and consists of an integrated system including the high temperature slagging incinerator, completed with the pretreatment line of incoming waste and the cleaning of the resulting off-gases.

The paper presents the state of the art of this original SCK/CEN-technology and gives the results of the tests done with special hazardous wastes.

INTRODUCTION

Relatively important volumes of solid and liquid wastes slightly contaminated with alpha and beta-gamma emitters are generated in almost all the activities connected with the nuclear fuel cycle. The best way to make these materials suitable for final disposal is through volume reduction and insolubilization

In the high temperature slagging incinerator (HTSI), most of the solid or semi-solid combustible and non combustible waste streams can be mixed together and directly converted to a stable leach resistant residue.

The existing HTSI-plant at Mol, has treated radioactive wastes from Belgian and foreign nuclear power plants, research centers, radioisotopes production plants, and radioisotope users. During many incineration tests of about 120 hours each, the most important characteristics of the process have been studied and it has been shown how the total decontamination factor of the off-gas cleaning system, the volume reduction factor, the quality of the resulting slag and so forth depends on the heat of combustion of the waste feed, its composition, the the melting point and the viscosity of the resulting slag.

In the meantime, exploratory research has been carried out to extend the range of the applications of the system. Possible users include :

- polyaromatic hydrocarbons such as dioxines
- polyhalogenated hydrocarbons such as PCB's and PCT's
- pesticides
- metal containing organic waste
- waste from genetic engineering laboratories
- military weapons discards
- waste products from chemical, pharmaceutical, petrochemical industries
- others

Finally, during the whole operation time, continuous research has been carried out about the recycling of granules to increase the mineral content of the waste, to concentrate the radioactivity in the granules, and to improve the volume reduction factor of the waste.

PURPOSE

The purpose of the research work done during the last ten years was to develop a total system for the incineration of different kinds of wastes. These waste streams all have in common that they respond to the following definition of toxic or hazardous industrial waste :

- waste which, due to the presence of special atoms like halogens, sulfur, nitrogen, phosphorus, etc. needs a high temperature for complete combustion
- waste which, due to the presence of non combustible materials, must be burned at high temperature above the melting point to obtain a liquid slag
- waste which, due to the presence of substances hard to combust (like polyaromatic hydrocarbons) needs to be burned at high temperatures to obtain a sufficiently high combustion efficiency
- waste which, due to the toxic characteristics, needs to be handled in an automatically

operated installation to protect the working people.

Therefore, this total system for incineration of wastes has to fulfil the following requirements :
- the system must be an integrated system
- the system must be remotely operational
- the incinerator has to be operated at very high temperatures, higher than the melting point of the non combustible fraction of the waste
- the system must contain a complete off-gas purification system for dust removal and for chemical products and radioisotopes
- the efficiency of this off-gas purification system must be very high.

APPROACH

Starting from an experimental furnace, the system built in Mol has been systematically worked out to become an integrated industrial demonstration plant. Depending on the waste feed composition, its capacity is around 60 kg/h.

Fundamental research as well as many experimental incineration runs were carried out to develop the general basic knowledge of incineration processes at high temperatures, and to gain expertise in the design, construction and operation of these type of total incineration processes.

A large part of the low active solid wastes and of particular liquid hazardous waste produced in Belgium and its neighbouring countries are treated in this HTSI-plant. During the incineration campaigns operational problems were encountered. Rather extended shutdown periods have been necessary for throughout maintenance of the installation or major improvements to the facility. The encountered problems are dealt with further on in the paper together with the proposed solutions and the improvements which have been carried out.

Recently more extensive exploratory research has been carried out on the incineration of special hazardous industrial wastes. The positive results obtained justified the development of larger capacity industrial units. This work has started in 1984 with computer code scaling-up calculations, the design, construction and operation of an industrial unit of 130 kg/h and the design of a unit of 400 kg/h. The latter will be used to incinerate in one single unit both low level radioactive waste as well as highly toxic hazardous industrial wastes. This installation will be ready in 1988 and will be built according to the HAWAI process.

RESULTS

The complete HAWAI-system consists mainly of :
- the incinerator itself
- the waste feeding system
- the granulator and its granules evacuation device
- the main oxygen burner with its feeding assemblies
- the auxiliary burner with its assemblies for feeding liquid wastes
- the off-gas purification assembly
- the instrumentation and remote operation and control systems
- the peripheral circuits and auxiliaries.

Description of the process

At the incineration plant, the wastes are stored in the storage area in the original package or in polyethylene bags after checking the packages for the presence of large metal pieces, explosives or high oxidation products.

Then the waste is fed to the shredder by means of conveyors. A weighing device ensures that a suitable feed composition is achieved within given margin.

The shredder reduces the waste to a size of 5 cm. The shredded waste pieces fall onto a conveyor which transfers them to mixing bins. The latter also provides buffer storage volume and enables the solid waste to be mixed with pastes or sludges before incineration. Screw feeders convey the blended waste from the mixing bins to the HTSI-incinerator.

The waste is loaded into an annular space between the outer wall of the furnace and an inner cylinder and is further pushed towards the combustion chamber. Then, the waste slides down to the outlet hole of the main combustion chamber and makes an inverted conical surface which delimits the combustion chamber at its lower part. The surface of the cone melts locally, forming an thin film of molten slag, flowing along the slope of the cone and leaving the main combustion chamber through the central outlet hole, together with the hot flue gas flow. The slag droplets fall into the granulator where they are quenched and burst to yield granules, while the combustion gas is channelled into the horizontal secondary combustion chamber. Here all the oxidation reactions are completed.

Downstream of the secondary combustion chamber the off-gases are cooled in a heat exchanger and by injection of water in an evaporative cooler. Dust is completely filtered out in classical bag filters followed by absolute HEPA-filters. In a scrubbing unit the gaseous oxidation products are absorbed according to the stack emission limits. An off-gas blower keeps the whole installation in underpressure.

The incinerator

The incinerator itself consists of three parts : the main combustion chamber, the outlet chamber, and the post-combustion chamber.

One of the original features of the HTSI-process is that the main combustion space is surrounded by a wall formed by very material to be treated. This space is a conical cavity formed in the bottom part of the main combustion chamber between the lower edge of an interior cylindrical wall and the slag outlet hole. The inner wall of that cylinder is lined with refractory material so as to form conical surface opposite to that in which the combustion takes place. The main burner is mounted at the top of this so-called "bell".

The waste is fed into the annular space between the outer shell of the furnace and the fixed inner cylinder. Rotating paddles and ploughs ensure progression of the feed material down to the top of the conical cavity, which is continuously fed.

The upper layer of the waste

cone is exposed to intense heat radiation from the main oxygen burner off-gas stream and from the combustion of the waste pyrolysis products. This radiation is reflected downwards by the bell and the whole forms a kind of cupola furnace. As a result of this, the non combustible residues from the waste are melted into a slag film flowing along the slope of the waste cone towards the central bottom hole. The waste pyrolysis gases flow through this viscous layer which acts as a liquid filter lowering the dust content of the non filtered off-gases down to maximum 30 mg/Nm^3.

Originally, the main burner was supplied with fuel and ambient air to promote combustion. Recently, this device had been replaced with an advance prototype using pure oxygen. The mean off-gas temperature out of the primary combustion chamber is therefore increased up to 1700° C. The surface of the waste cone reaches under those working conditions a temperature between 1450 and 1650° C.

The outlet chamber is located under the common outlet hole for the molten slag and the off-gases. The bottom of this chamber is fitted with an outlet dipping into the water pool of the slag catching unit, the so-called granulator. The molten slag and the off-gases are separated from each other in this chamber.

In the post-combustion chamber, the off-gases are mixed with the steam produced in the granulator and with the secondary air. It is equipped with an auxiliary burner working with waste oil. Injection systems for waste liquids are mounted around this waste burner. The combustion air is enriched with oxygen and the possibility exists to inject pure oxygen in the flame to obtain a very high flame temperature.

Slag extraction

The slag is quenched in water, yielding very irregularly shaped granules with a basalt like appearance.

Due to the high incineration temperature, this product has excellent properties for safe disposal. The residues from incinerated materials are concentrated in a small volume and trapped in an amorphous matrix consisting mainly of silica, alumina, iron(2)-oxide, alkaline earths and oxides of the other metals present in the original waste materials. The true density has a mean value of 3300 kg/m^3, the Vickers microhardness is in the range of 500 10(exp7) Nm/m^2, the global leaching rate based on the most significant elements varies from
10(exp-7- to 10(exp-5) $\text{g/cm}^2\text{/day}$.

The grain size distribution of the product is :

$\varnothing > 5.0$ mm : 21 wt.%
$2.5 < \varnothing < 5.0$ mm : 27 wt.%
$2.0 < \varnothing < 2.5$ mm : 13 wt.%
$1.0 < \varnothing < 2.0$ mm : 26 wt.%
$0.5 < \varnothing < 1.0$ mm : 8 wt.%
$\varnothing < 0.5$ mm : 5 wt.%

The melting point varies between 1200 and 1500° C according the chemical composition.

Secondary wastes

The only secondary waste stream generated during this process is the granulated basaltic material called slag. Indeed, the quenching effluents and scrub solutions are adequately treated and the resulting concentrates are fed back into the furnace together with fly ash suitable modified after collection on the bag filters, the prefilters and the HEPA-air filters.

Incineration efficiency

The incineration efficiency depends on many parameters such as incineration temperature, residence time and spread on residence time, the mixing rate of fuel and oxidant, the chemical substances participating in the reactions etc.

The interdependence of the reaction rate and the temperature can be determined by the typical Arrhenius equation

$$k = A.e(\exp -E/RT)$$

where :

k = reaction rate
E = activation energy (enthalpy)
R = the gas constant
T = the absolute temperature
A = a constant factor.

Kinetic data of the incineration of waste products can rarely be found. Reed (1) has collected some results from a number of tests and research and development studies on the destruction of hazardous materials. Mean values of the rate constant can be calculated fom some typical waste products such as polyhalogenated hydrocarbons (PCB's).

During special test runs the combustion efficiency for a wide range of chemical substances was determined. Tests were done with polychlorobyphenyl, chlorinated derivation products from toluene, solid chlorinated wastes such as PVC(polyvinylchloride)-containing solid waste, phosphorous containing waste, etc.

The tests were always characterized by the following operational parameters :

- temperatures at different locations in the combustion chambers
- chemical analysis of the off-gases
- flow rates of incoming products
- flow rates of off-gases
- residence time.

As an example the results of an incineration run for PCB's at moderate temperature are given in table 1.

Table 1 : Experimental test results of PCB's incineration

mass flow rate of PCB	248 g/h
air flow rate	1222 Nm^3/h
off-gas flow rate	1272 Nm^3/h
% H_2O in off-gases	7.81 %
% CO_2 in off-gases	8.47 %
% N_2 in off-gases	75.91 %
PCB mass flow rate in off-gases	0.55 mg/h
residence time	1.92 sec
combustion temperature	957° C
lambda air factor	1.635
off-gas O_2 concentration	7.8 %
combustion efficiency	99.99977 %

This high incineration efficiency is achieved at moderate temperature (957° C) due to the following facts :

- high oxygen amount in the off-gases
- good vaporization of the liquid waste which was done with a special device whereby the liquid waste is vaporized in droplets of 50 to 100 micron diameter
- the good contact between waste and oxidant due to high mixing effect in the flame.

The combustion efficiency is

calculated as the destruction efficiency for PCB. One should have in mind that a high destruction efficiency of the waste product is not sufficient. In case of too low incineration temperatures or too low residence times, highly toxic partial oxidation products can be formed in the off-gases, resulting in an overall very bad process. Therefore the off-gases should be analyzed completely and one should look for PCDD, PCDF, and others.

In the test mentioned above all important harmful substances were present in the off-gases at concentrations lower than the detection limits. Analyses were done for PCDD's (tetra, penta, hexa, hepta, octa isomeres) and for PCDF's (tetra, penta, hexa, hepta and octa isomeres).

In practical conditions where the incineration conditions are not always optimal, it is to be preferred to operate the incinerator at a very high temperature, to be sure that all hazardous materials are completely oxidized, even in case of poor vaporization. The HTSI-furnace as part of the new HAWAI-process will have following operational conditions and corresponding oxidation efficiencies :

Table 2 : HAWAI operational conditions

main combustion chamber	
flame temperature	> 2000° C
residence time at T	0.1 sec
mean temperature in the combustion chamber	1700° C
mean residence time at T	0.5 sec
corresponding efficiency	99.2 %
outlet chamber	
temperature	1300° C
residence time	0.5 sec
corresponding efficiency	93.7 %
post-combustion chamber	
temperature in 1st zone	1700° C
residence time at T	1 sec
corresponding efficiency	99.99 %
temperature in 2nd zone	1300° C
residence time at T	1 sec
corresponding efficiency	99.6 %
overall efficiency of the global system : 99.99999998 %	

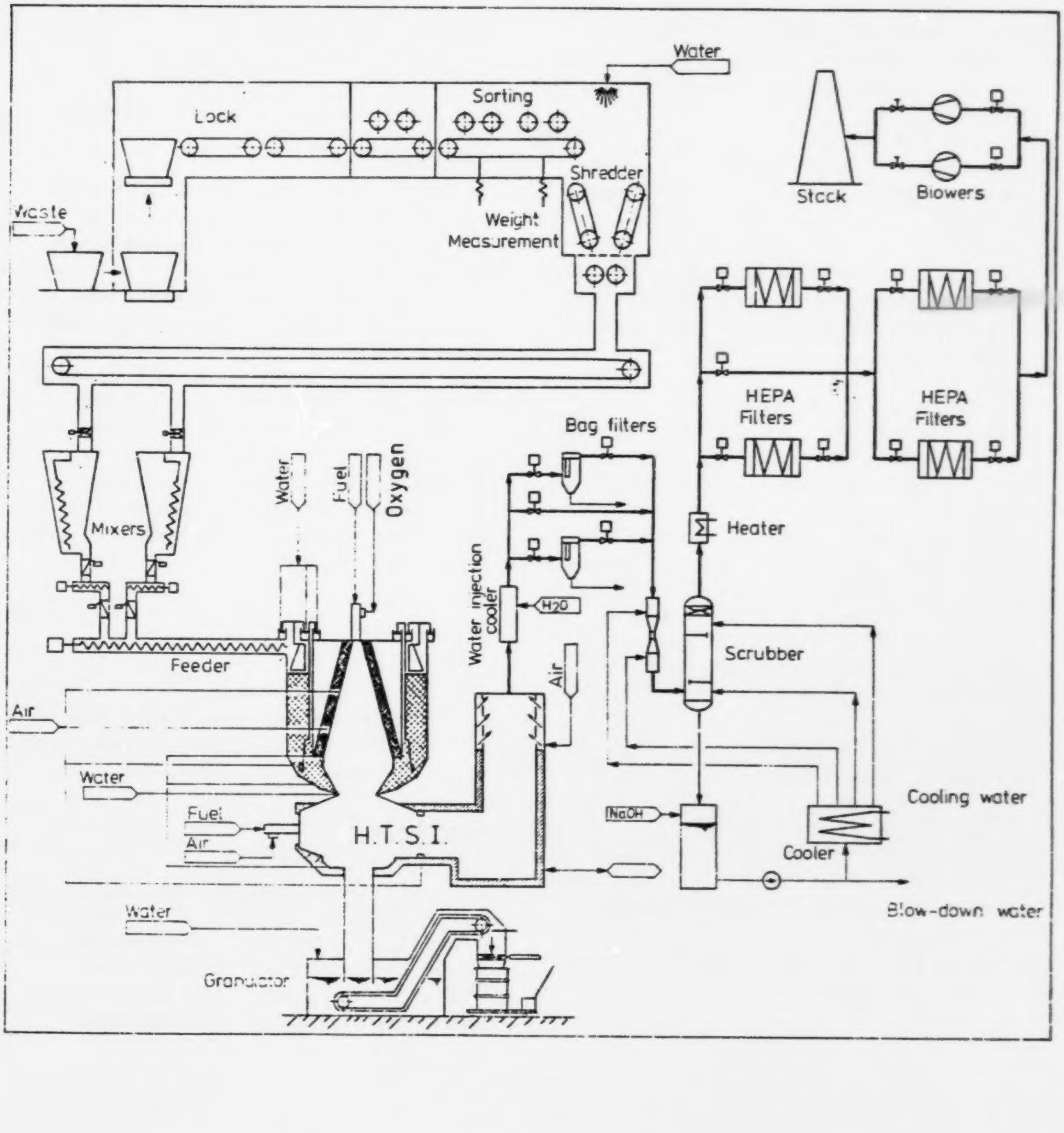
This means that at this moment the HAWAI-system is the only one with such high operating temperatures and corresponding operational features, which has reached the industrial application phase. At Mol in Belgium the first plant is in operation since 1976 and working partly according the conditions of table 2. From 1989 on a second industrial installation will be operational for both low level radioactive waste and industrial hazardous waste, which can be solid, liquid or sludges.

REFERENCES

(1) Reed, J.C., Moore, B.L. Ultimate hazardous waste disposal by incineration. Toxic and hazardous waste disposal.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.


Water
Lock
Sorting
Shredder
Stack
Blowers
Waste
Weight Measurement
HEPA Filters
HEPA Filters
Bag filters
Water
Fuel
Oxygen
Mixers
Heater
Water injection cooler
H2O
Air
Scrubber
Feeder
Air
Water
Fuel
Air
H.T.S.I.
NaOH
Cooling water
Cooler
Blow-down water
Water
Granulator

PCB TRIAL BURN IN A MODULAR, MOVABLE INCINERATOR

Prakash Acharya
ENSCO Environmental Services (ENSCO)
White Bluff, TN 37187

ABSTRACT

ENSCO conducted a trial burn from March 11-13, 1986, in El Dorado, Arkansas, of an MWP-2000 Modular Incinerations system to destroy PCB liquids, PCB items and PCB-contaminated solids in conformance with TSCA requirements. MWP-2000 has 4 main process modules--Rotary kiln, capable of destroying liquid PCBs and PCB-contaminated dirt; secondary combustor, capable of destroying high-level PCB liquids; heat recovery system, generating steam to drive the system's prime mover; and pollution control system that removes acid gases and fine particulates from the gas stream. The trial burn consisted of 5 separate tests. The first 3 tests were replicate tests. In these tests PCB-contaminated soils, having a PCB content of 1.8%, and PCB-contaminated fuel, having a PCB content of 2.9% were burned in the kiln, while high level PCB liquids, having a PCB content of 60%, were burned simultaneously in the secondary combustor. In the fourth test, PCB liquids, having a PCB content of 61%, were burned in the secondary combustor while the kiln was not operated. In the fifth test, pre-shredded capacitors having a PCB content of 18% were fed to the kiln and PCB liquids having a PCB concentrations of 64%, were fed to the secondary combustor. Trial burn results clearly demonstrate that a DREs of 99.999999% were achieved. HCl removal efficiencies of 99.9% were achieved. Total particulate emissions of 0.01-0.02 gr/DSCF were achieved. PCB contamination in the kiln ash and effluent residuals of <2 ppm were achieved.

Trial Burn Plan

The demonstration burn plan (trial burn plan) consisted of five separate tests. The first three tests (trial burn #1) were replicate tests. In these tests PCB-contaminated soils, having a PCB content of approximately 5.5%, and PCB-contaminated fuel, having a PCB content of approximately 4.5%, were burned in the rotary kiln (Fig. 1). At the same time, high-level PCB liquids, having a PCB content of approximately 46%, were burned simultaneously in the secondary combustor. The purpose of these three tests was to demonstrate the capability of the system to (1) achieve 99.9999% PCB destruction and removal efficiency (DRE); (2) handle solid and liquid wastes in the kiln and liquid wastes in the secondary combustor; (3) remove PCBs from contaminated soils; and (4) produce a scrubber effluent having less than 2 ppm PCB.

In the fourth test (trial burn #2), high-level PCB liquids, having a PCB content of approximately 46%, were burned in the secondary combustor while the kiln was not operated. The purpose of this test was to demonstrate that a 99.9999% PCB destruction and removal efficiency and a scrubber effluent PCB concentration of less than 2 ppm could also be achieved when the secondary combustor was operated without the kiln.

In the fifth test (trial burn #3), pre-shredded capacitors, having a PCB content of approximately 38%, were fed to the kiln and high-level PCB liquids, having a PCB concentration of approximately 46%, were fed to the secondary combustor. The purpose of this test was to demonstrate that (1) a 99.9999% PCB destruction and removal efficiency and a scrubber effluent PCB concentration of less than 2 ppm could be achieved when burning capacitors in the kiln and PCB liquids in the secondary combustor; (2) the kiln could handle shredded capacitors; and (3) a detoxified kiln ash could be achieved when burning capacitors.

An independent contractor was hired to sample and analyze stack gas emissions. Each test was divided into two portions. In the first portion, which took approximately one hour, stack emissions were sampled for HCl, particulate, O2, CO2, NOx and SOx. In the second portion, which took approximately four hours, stack emissions were sampled for PCBs, PCDDs (dioxins), PCDFs (dibenzofurans) and Chlorinated Organics. Solids/Ash and scrubber effluent generated during the tests were sampled and analyzed for PCBs, PCDDs and PCDFs. All wastes, contaminated fuel, and clean fuel were sampled then analyzed for PCB, BTU and Chlorine content by the in-house personnel.

Process Description

The modular waste processor (MWP-2000) has four main process modules; (1) Rotary Kiln, (2) Liquid Incinerator/Secondary Combustor, (3) Heat recovery system, and (4) Pollution control system. A process flow diagram is presented in Figure 1.

The rotary kiln is a refractory lined, carbon steel cylinder mounted horizontally on a trailer and rotated by a trunnion drive mechanism. Contaminated solids are transported by belt conveyor to a charging hopper at the front of the kiln. A screw feeder at the bottom of the hopper feeds the solids into the front of the kiln at a controlled feed rate. Kiln outlet gas temperature is maintained around 1700 degrees F to assure vaporization and partial destruction of organic constituents. Solids residence time of approximately 30-40 minutes and kiln rotation of 2-3 rpm are maintained to ensure complete mixing and sufficient burn time for the solids. Residual ash drops out of the back end of the kiln into a water sealed ash receiving tank and is transported by a chain drag conveyor to a portable ash storage bin where it is sampled for potential contaminates before being sent to landfill.

The liquid incinerator/secondary combustor is a large refractory lined shell sized to provide a combustion gas residence time of 2 seconds at a temperature exceeding 2200 degrees F. PCBs and other hazardous liquids are destroyed in the primary burner that completes the incinerator/secondary combustor assembly. This burner has the capability to burn highly chlorinated materials with low BTU values. The primary combustion products mix with the kiln off gas and additional air in the secondary combustor. The design of the system allows a range of combinations of kiln off gas, secondary waste to be destroyed. The variations are governed by the thermal inputs imposed by the various waste streams.

A trailer mounted fire tube boiler is provided to recover heat from the gas leaving the secondary combustor. The waste heat boiler provides the steam required for the system prime mover. A boiler feed water treatment package is included to assure minimal boiler fouling and subsequent boiler maintenance. A deaerator is provided for oxygen removal and feed water heating. Off gases from the waste boiler are drawn through an Inconnel elbow where the hot gas is sprayed with quench recirculation solution. The off gases are cooled to saturation before reaching the exit of the quench elbow.

A Fiber Reinforced Plastic sump box drains all the solution into a large neutralization tank where a sufficient amount of lime is added to neutralize the acid solution. This neutralization tank not only acts as the sump for the Quench recirculation pump, but also provides the scrubbing medium for the packed tower which removes the bulk of the acid gases from the quenched off gas stream.

The steam from the boiler is used to drive an ejector/scrubber system. The steam ejector/scrubber acts not only as the system prime mover, but also as a final pollution control device. The quenched and scrubbed gases containing small amounts of particulates and HCl are drawn through the ejector nozzle. The turbulence created by the unique nozzle and mixing tube arrangement causes efficient particulate capture well into the submicron range. The water, after removal of agglomerated particulate, is recycled to the steam ejector scrubber. A small, continuous purge is maintained from the scrubber sump to keep the solids concentration from building up in the scrubber recirculation stream.

A state-of-the-art support laboratory is provided for rapid chemical and heating value analyses of the waste materials. The laboratory is equipped with an atomic absorption spectrophotometer for metals analyses and a gas chromatograph for analyses of volatile organics and other organic priority pollutants. The control room is also located in the laboratory van. The incinerator combustion process, ancillary processes, and stack gas quality are continuously monitored by a microprocessor system for instant analysis of process conditions. In the event that critical process parameter specifications are not met, the computer automatically ceases waste feed operations and switches to clean feed until the problem has been resolved.

Test Conditions

Waste Characteristics

The high-level PCB liquids that were fed to the Secondary Combustor in all five tests and that were used to formulate the PCB-contaminated soil and fuel used in the first three tests were liquids that had been drained from non-mineral oil transformers at ENSCO's transformer decommissioning facility. The PCB, Chlorine and BTU contents of these liquids, as determined from composite samples collected during each test are presented in Tables 1 and 2. The PCB content of the high-level PCB liquids averaged 61% (Table 1) versus the anticipated 46%. Also, the chlorine content of these liquids averaged 43% (average of the first three HCl/particulate part of the test--Table 2) versus the anticipated 40%.

The PCB-contaminated fuel fed to the kiln burner in the first three tests of Trial burn #1 was formulated by mixing 63% (by.wt.) of the high-level PCB liquids with 37% (by.wt.) of clean fuel in a storage tank. The resulting mixture was kept mixed by recirculating pumps. The PCB, chlorine and BTU contents of this mixture, as determined from composite samples collected during each test are presented in Tables 1 and 2. The PCB content of this mixture averaged 29% (Table 1) versus the planned 4.5%. This higher content was formulated to offset, in part, the lower-than-planned introduction of PCBs to the kiln via the feed of PCB-contaminated soils which could be fed at a rate of only 4000 lb/hr rather than 8000 lb/hr (because of the kiln's physical limitation at the time of the test). For the same reason, the chlorine content of the mixture averaged 20% (Table 2) versus the planned 4.5%.

The PCB-contaminated soil fed to the kiln in the first three tests was formulated by mixing 12% of high-level PCB liquids with 88% of moist, clean sandy soil. The mixture used in each test was formulated several hours before the test and properly stored. The PCB, chlorine and BTU content of the mixture as determined from composite samples collected during each test are presented in Tables 1 and 2. The PCB content of the mixture averaged 1.8% (Table 1) versus the planned 5.5%. This lower contamination level was formulated to avoid creating a mixture having free liquids. Also, for the same reason, the chlorine content of the mixture averaged 3.6% versus the planned 4.8%.

The PCB capacitors fed to the kiln in Test 5 were pre-shredded at ENSCO's El Dorado facility, placed in 30-pound fiberboard drums and stored in a warehouse until just before the initiation of the test. The calculated PCB and chlorine contents (Table 2) of the capacitor feed was 18% and 10.2% respectively were less than the anticipated values of 36% and 16%.

Waste Feed Rates

The computer logged the waste feed rate for every 15 minutes during the test. The computed waste rate is the average of all the 15 minute waste rate readings for that part of the test. Separate waste rates are computed for the HCl-particulate part of the test and the DRE part of the test. The waste rates are presented in Table 3.

Total PCB and Chlorine Feed Rates

Total PCB and total chlorine feed rates to the system were calculated using waste characterization data (Tables 1 and 2) and using the waste feed rates (Table 3). These totals are presented in Table 4.

CONCLUSIONS

The trial burn results (Table 6) clearly demonstrate the outstanding performances of the unit.

a) DREs of 99.999999% were achieved, when PCB containing wastes are incinerated. ENSCO also conducted another trial burn using surrogate wastes demonstrating that the MWP-2000 can achieve 99.9999% DRE when burning predominantly organic manufacturing and formulating processing wastes that are included among the F020-F)27 wastes. The TSCA and RCRA trial burn results show that the MWP-2000 is capable of incinerating a broad range of hazardous wastes and hazardous constituents. The results of the RCRA trial burn is not included in this paper.

b) HCl removal efficiencies of 99.9% were achieved. Table 4 indicates that the chloride loading to the system was in the range of 600-1000 lb/hr. ENSCO also tested the HCl scrubbing system up to a chloride loading of 1300 lb/hr and HCl removal efficiency of 99.9% were achieved.

c) Total particulate emissions of 0.01-0.02 gr/DSCF were achieved when soil throughput to the kiln was in the range of 2000-4000 lb/hr. Recent test results indicate that the total particulate emissions of 0.01-0.02 gr/DSCF could also be achieved when soil throughput to the kiln was 8000-12000 lb/hr.

d) Total dioxins through the stack gas was below the detection limit of the instrument.

e) PCB contamination in the kiln ash and effluent residuals of less than 2 ppm were achieved.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

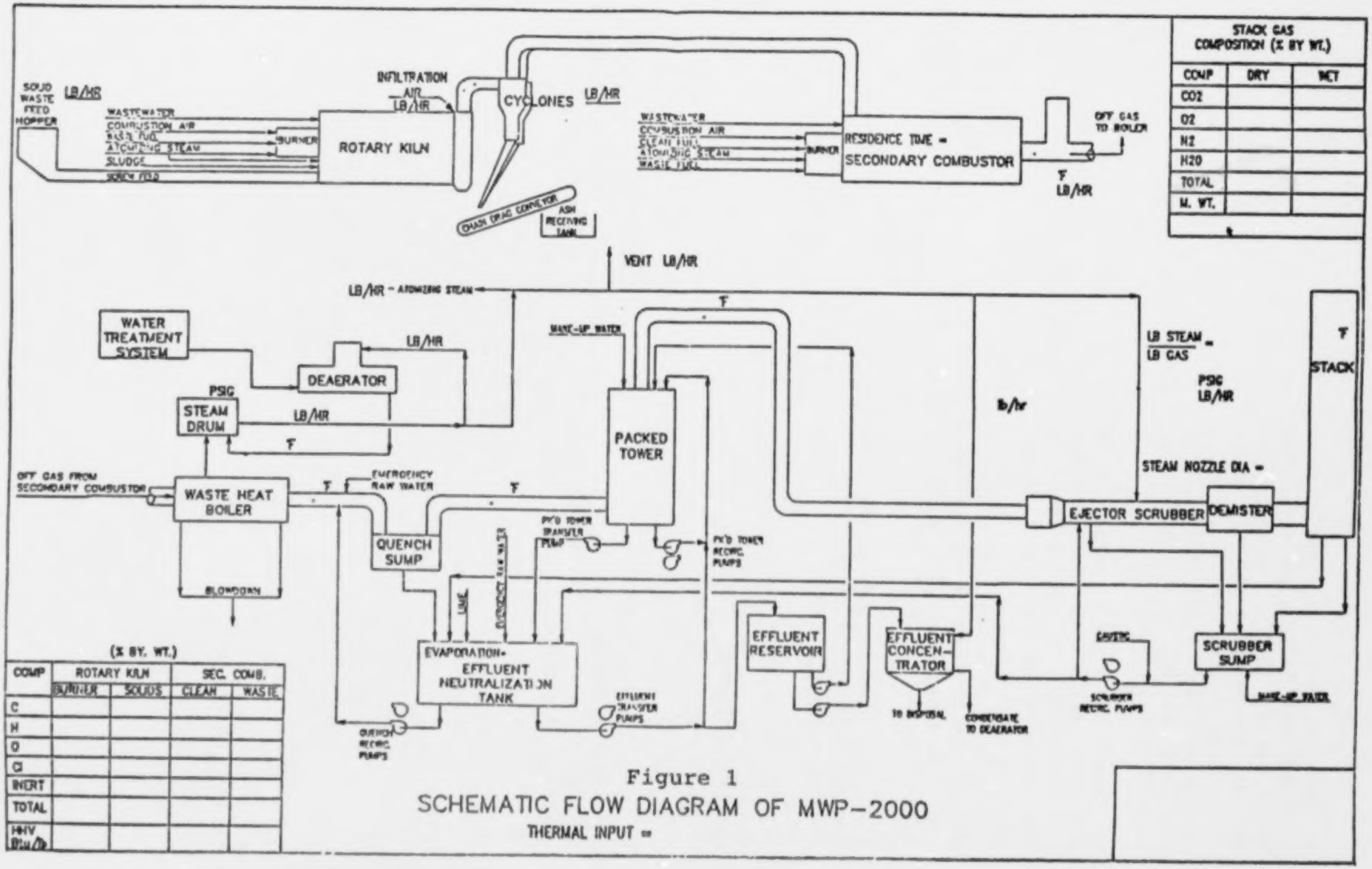

SOLID WASTE FEED HOPPER
LB/HR
WASTEWATER
COMBUSTION AIR
BASE FUEL
ATOMIZING STEAM
SLUDGE
SCREW FEED
BURNER
ROTARY KILN
INFILTRATION AIR LB/HR
CYCLONES LB/HR
CHAIN DRAG CONVEYOR
ASH RECEIVING TANK
WASTEWATER
COMBUSTION AIR
CLEAN FUEL
ATOMIZING STEAM
WASTE FUEL
BURNER
RESIDENCE TIME - SECONDARY COMBUSTOR
T LB/HR
OFF GAS TO BOILER
STACK GAS COMPOSITION (% BY WT.)
COMP
DRY
WET
CO2
O2
N2
H2O
TOTAL
M. WT.
VENT LB/HR
LB/HR - ATOMIZING STEAM
WATER TREATMENT SYSTEM
DEAERATOR
LB/HR
PSIG
STEAM DRUM
LB/HR
T
OFF GAS FROM SECONDARY COMBUSTOR
WASTE HEAT BOILER
BLOWDOWN
T
EMERGENCY RAW WATER
T
MAKE-UP WATER
T
PACKED TOWER
QUENCH SUMP
PK'D TOWER TRANSFER PUMP
PK'D TOWER RECIRC. PUMPS
LIME
EMERGENCY RAW WATER
EVAPORATION-EFFLUENT NEUTRALIZATION TANK
QUENCH RECIRC. PUMPS
EFFLUENT TRANSFER PUMPS
EFFLUENT RESERVOIR
EFFLUENT CONCENTRATOR
TO DISPOSAL
CONDENSATE TO DEAERATOR
lb/hr
LB STEAM / LB GAS =
PSIG
LB/HR
STEAM NOZZLE DIA =
EJECTOR SCRUBBER
DEMISTER
T
STACK
CAUSTIC
SCRUBBER RECIRC. PUMPS
SCRUBBER SUMP
MAKE-UP WATER
(% BY. WT.)
COMP
ROTARY KILN
BURNER
SOLIDS
SEC. COMB.
CLEAN
WASTE
C
H
O
Cl
INERT
TOTAL
HHV Btu/lb

Figure 1

SCHEMATIC FLOW DIAGRAM OF MWP-2000

THERMAL INPUT =

Table 1. PCBs in Liquid Fuel/Contaminated Solids/Ash/Effluent Water

Burn and Test Numbers	Test	Kiln Waste/Ash		Sec. Combustor Waste			
		PCB-Contaminated Soil	PCB-Contaminated Fuel	Kiln Ash (ppm)	High-level PCB Liquids	Clean Fuel (ppm)	Effluent Water (ppm)
Burn 1 Test 1	HCl Particulate	1.69	26.6	<2	45.0	---	<2
	DRE	2.34	26.6	<2	58.2	---	<2
Burn 1 Test 2	HCl Particulate	1.69	26.6	<2	45.0	---	<2
	DRE	1.44	32.7	<2	60.7	---	<2
Burn 1 Test 3	HCl Particulate and DRE	1.68	27.6	<2	61.5	32.3	<2
Burn 2 Test 4	HCl Particulate and DRE	---	---	---	60.9	---	<2
Burn 3 Test 5	HCl Particulate and DRE	18.00[a]	---	15	64.0	11.7	<2

[a] PCB content of shredded capacitors

PCB contents are in (%by.wt) unless otherwise specified
Total PCDDs and total PCDFs in each of the kiln ash and effluent water samples were below the detection limit of the instrument.

Five tests were conducted. Each test was divided into two parts. Of the two portions of the tests, the first part was HCL/Particulate and the second portion was DRE part. Each test is a continuous run but there is a variation in the PCB concentrations.

Table 2.

Heating Value and Chlorine Contents in the Liquid Wastes/Contaminated Solids

Trial Burn Test Number	Test	Kiln Waste				Secondary Combustor Waste	
		PCB-contaminated Fuel		PCB-contaminated Soil		High-level PCB liquids	
		Chlorine %by.wt.	HHV BTU/lb	Chlorine %by.wt.	HHV BTU/lb	Chlorine %by.wt.	HHV BTU/lb
Burn 1 Test 1	HCl Particulate	21.23	15000	3.90	1290	34.46	12140
	DRE	19.70	15100	4.13	1100	49.33	9500
Burn 1 Test 2	HCl Particulate	21.23	15000	3.90	1290	34.46	12140
	DRE	18.17	13160	3.14	800	47.54	9500
Burn 1 Test 3	HCl Particulate	20.85	14800	3.10	1100	48.49	8800
	DRE	20.85	14800	3.10	1100	48.49	8800
Burn 1 Test 4	HCl Particulate	---	---	---	---	49.36	9400
	DRE	---	---	---	---	49.36	9400
Burn 3 Test 5	HCl Particulate	---	---	10.20[a]	6900[a]	47.28	9400
	DRE	---	---	10.20[a]	6900[a]	47.28	9400

[a] Estimated for shredded capacitors.

HHV--Higher Heating Value

Table 3. Waste Rates

HCl-Particulate Test[a] /DRE Test[b]

WASTE	Trial Burn #1 Test 1[c]	 Test 2[c]	 Test 3[c]	Trial Burn #2 Test 4[c]	Trial Burn #3 Test 5[c]
PCB-Contaminated Soils Flow to Kiln (lb/hr)	2370 a 4174 b	4074 3331	3530 4059	---	---
Shredded PCB Capacitors to Kiln (lb/hr)	---	---	---	---	902 751
PCB-Contaminated Fuel to Kiln Burner (lb/hr)	425 261	283 297	330 291	---	---
High-level PCB Liquid to Secondary Combustor (lb/hr)	1796 1722	1616 1706	1718 1727	1901 2110	1061 1062

a HCl-Particulate test was for one hour.

b DRE test was for four hours.

c Each test consisted of HCl-Particulate test and DRE test, totalling five hours of sampling time.

Table 4. Summary of PCBs and Chlorides

Trial Burn		Total PCBs to the system	Total PCBs through Stack	Total Chlorides to the System	Total Chlorides through Stack
Trial Burn 1	Test 1	1170	5.9×10^{-6}	802.0	0.779
	Test 2	1181	4.6×10^{-6}	775.9	0.939
	Test 3	1211	2.96×10^{-6}	1011.3	0.703
Trial Burn 2	Test 4	1285	5.38×10^{-6}	938.3	0.846
Trial Burn 3	Test 5	815	11.95×10^{-6}	593.6	0.076

* All flow rates are in lb/hr.

Table 5. Summary of Critical Operating Conditions During the Tests

	TEST CONDITION				
	TRIAL BURN #1			TRIAL BURN #2	TRIAL BURN #3
PARAMETER	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5
FEED TO SYSTEM					
PCB-Contamineated soil feed rate to the kiln (lbs/hr)	2370	4074	3530	---	---
Shredded PCB capacitors to the kiln (lbs/hr)	---	---	---	---	902
PCB-Contaminated fuel to kiln burner (lb/hr)	425	283	330	---	182[a]
High-level PCB liquids/ clean fuel to sec. comb. (lb/hr)	1796/ 572	1616/ 578	1718/ 561	1901/ 462	1061/ 579
Total heat input to the system (MM Btu/hr)	42.37	40.4	34.64	36.11	30.92
OPERATING CONDITIONS					
Kiln outlet gas temperature (degree F)	1628	1515	1688	710	2052
Secondary combustor outlet gas temp. (F.)	2310	2352	2386	2404	2361
Gas residence time in sec. combustor (sec)	1.75	1.78	2.02	1.84	2.04
Stack flow rate (DSCFM)	7342	6800	6072	6586	6180
PERFORMANCE INDICATORS					
Oxygen concentration in stack gas (% by vol.) (dry basis)	4.6	5.7	4.6	8.7	5.0
Carbon monoxide in stack gas (ppm) (dry basis)	2	3	5	4	3
Carbon dioxide concentration in stack gas (% by vol.) (dry basis)	13.4	12.8	13.8	11.4	13.0

[a] During Test 5, clean fuel was used.

Table 6. Summary of Test Results

	TEST RESULT				
	TRIAL BURN #1			TRIAL BURN #2	TRIAL BURN #3
PARAMETER	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5
Destruction and Removal Efficiency: DRE (%) (overall) PCBs	99.999999	99.999999	99.999999	99.999999	99.999998
Particulate concentration in stack gas corrected to 7% oxygen (gr/DSCF)	0.0105	0.0239	0.0151	0.0252	0.0117
Acid gas scrubbing efficiency: (%)	99.90	99.88	99.93	99.91	99.99
Nox concentration in stack gas: (lb/hr)	2.26	2.12	2.39	3.31	2.39
SO2 concentration in stack gas: (lb/hr)	<0.2	<0.2	<0.2	<0.2	<0.2
Total chlorinated organics (Rcl)(lb/hr)	0.0353	0.0364	0.0168	0.0386	0.0309
Chlorinated benzene (lb/hr) x 10^{-3}	<0.009	<0.035	<0.009	<0.009	<0.011
Chlorinated Phenol (lb/hr) x 10^{-3}	<0.058	<0.015	<0.022	<0.039	<0.022
Dioxins/Furans:					
Dioxins (lb/hr) (2,37,8-TCDD, total tetra, total PCDD)	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L
Furans (lb/hr)					
2,3,7,8-TCDF	2.33	3.85	2.7	1.4	12.0
Total tetra x 10^{-8}	28.0	6.25	4.8	1.4	41.8
Total PCDF	99.1	38.1	14.5	1.4	234.1

B.D.L.: Below Detection Limit--Detection Limit for 2,3,7,8 TCDD--1.6×10^{-8} lb/hr
Total Tetra --1.6×10^{-8} lb/hr
Total PCDD --9.9×10^{-8} lb/hr

*Five different tests were conducted and each of the above number represents the result for the entire system as a whole.

*Acceptable limit for total Particulates is 0.08 gr/DSCF. Acceptable limit for DRE is 99.9999%. (Overall)

EXTRACTIVE METHODS FOR SOIL DECONTAMINATION;
OPERATIONAL TREATMENT INSTALLATIONS IN THE NETHERLANDS

J.W. Assink
Dutch Organization for Applied Scientific Research (TNO)
P.O. Box 342, 7300 AH APELDOORN, NETHERLANDS

ABSTRACT

In a general introduction to extractive methods attention is given to the basic principles, the potential fields of application and the costs of methods for treating contaminated soil.

The operational installations for extractive treatment in the Netherlands as well as some recent developments are described in the second part of the paper.

INTRODUCTION

This paper deals with the cleaning of excavated soil by means of extraction. The extractive methods include those by which contaminants are transferred to and carried off by a liquid phase. The following topics are discussed:

- A general description of the extraction process
- Field of application
- Available installations and state of the art in the Netherlands
- Costs of the cleaning method.

GENERAL DESCRIPTION OF THE EXTRACTION PROCESS

Two principal removal mechanisms may be distinguished in extractive cleaning (1, 2, 3, 4):

- The contaminants are dissolved in the extracting agent, with or without the assistance of a chemical reaction preceding or acting simultaneously with the extraction.
- The contaminants are dispersed in the extraction phase in the form of particles (suspended or colloidal), with or without the assistance of prior mechanical treatment. The subsequent separation between the contaminated particles and the relatively clean soil particles in the slurry is to be based on differences in:
  . particle size (sieving or classification)
  . settling velocity and/or specific density (wet classification or sink/float techniques).
  . surface properties (selective coagulation or flotation*))
  . combinations of these properties.

Since contaminants are often largely adsorbed to clay particles and humus, moderate to fair cleaning may result whenever these clay fractions and humus are separated from the soil by classification.

Aqueous extracting agents are usually preferred to organic extracting agents; this preference is based on a large number of considerations, such as:

---

*) flotation is not extensively discussed in this paper.

Preceding page blank

- Safety of the extracting agent for man and environment
- Prevention of additional groundwater and air pollution
- Natural presence of water in the soil
- Purification possibilities of loaded extracting agent
- User friendliness
- Costs.

A number of aqueous extracting agents may be distinguished. Besides water, the addition of chemicals aimed at improving the extraction efficiency may be considered.
Among the chemicals that may be added are:

- Acids, such as HCl, H_2SO_4 and HNO_3; the primary purpose of these acids is to dissolve contaminants, such as heavy metals.
- Bases, such as Na_2CO_3 and NaOH; the purpose of these substances is either to dissolve or disperse contaminants in the extraction phase. Especially clay and humus, usually containing a large quantity of contaminants, are easily dispersed in a NaOH-solution.
- Surface active agents; addition of these agents facilitates dispersion, for example of oil. Surface agents also play an essential part in flotation processes.
- Sequestering agents (complex formers), such as citric acid, NTA and EDTA; these substances will mainly complex the potentially "available" fraction of inorganic contaminants and will therefore minimize the adverse effects of the contaminated soil to the ecosystem.

In addition to the separate use of the above-mentioned chemicals, combinations thereof may be considered. The extraction process may also be favorably influenced by elevating the extraction temperature, or by prior oxidation of the contaminants with the assistance of an oxidizer (e.g. hydrogen peroxide or ozone).

A large number of physical, chemical and biological purification methods are practically available to clean the contaminated aqueous extracting agents that have resulted from soil cleaning. In practice, coagulation, flocculation followed by sedimentation or flotation are often used. However, other techniques (such as aerobic and anaerobic biological purification, ion exchange, electrolysis and membrane filtration) may be equally considered. These methods are extensively used in industry. For more information on this subject, the general literature is referred to.

POTENTIAL FIELD OF APPLICATION

Types of Soil

The extraction process is best suited for the cleaning of sandy soils low in humus and clay content; it is fairly easy to separate sand particles larger than 30-60 μm from the extraction fluid because of their relatively high settling velocity. Separation may be achieved by using relatively simple separation equipment, such as settlers and hydrocyclones. A second reason why the extraction process is highly suitable for the cleaning of sandy soil is that sand particles have a relatively small specific surface area; thus the amount of contaminants adsorbed to the sand particles after cleaning is relatively low.

Other types of soil (e.g. loamy soil, clay, peat and former waste dumping sites) are generally much more difficult to clean by extraction than sandy soil. Humus-like components, silt and clay particles readily form a relatively stable suspension with the extraction liquid. This is especially true for aqueous extracting agents with a high pH. By using methods based on classification these fines end up in a residual sludge which has te be properly disposed of. Because the costs for the treatment itself as well as for the disposal of relatively large quantities of hazardous residual sludge will be very high, classification is seldom an economically feasible method for non-sandy soils. Furthermore, many types of contaminants are readily adsorbed by humus and clay particles. By using methods based on dissolving contaminants the number of extraction steps or the amount of extracting agent required for a sufficient cleaning may be prohibitive to a feasible process.

Contaminants

Table 1 gives a survey of the potential applicability of extractive methods concerning the different kinds of contaminant in sandy soils. Not every given indication of applicability has yet been proven; therefore the table should be considered provisional.

The term "applicable" does not always imply that a contaminated site will be cleaned to a satifactory extent. Table 1 only refers to the technical applicability.

As may be concluded from table 1, extractive methods are applicable to virtually every type of contaminant, if only the appropriate method and process conditions are chosen and can be realized.

The actual applicabilities of the extractive methods do not solely depend on their technical ability to remove contaminants. Other factors that influence the selection of a certain method are:

- costs of cleaning up.
- equipment involved and complexity of the system.
- safety of the method (health risks, explosion risks etc.).
- environmental impacts (especially in case of organic extracting agents).
- waste streams (e.g. possibilities for the final disposal of residual sludge).
- possibilities of reuse of the cleaned soil.
- desired degree of contaminant removal, i.e. ability to meet applicable standards.

As to the last factor it should be remarked that the removal efficiency obtained so far in the operational installations seldom exceeds 99%.

The costs of cleaning a given quantity of soil depend on many factors, the principal ones being:

- depreciation of, and interest in the investment in the treatment installation.
- costs of labor.
- demand for chemicals and energy.
- costs of analyses for the purpose of process control.
- disposal of residual sludge (amount and type of sludge).
- the standards which the cleaned soil and waste water should meet.

Table 2 gives a qualitative indication of the amount of residual sludge, the demand for chemicals and the estimated range of the costs involved in the various extractive methods.

The given costs of cleaning are exclusive of costs involving the excavation and transportation of the soil. In view of the lack of sufficient practical data, the estimated costs should be regarded as approximations.

Table 1: Potential applicability of some extractive methods for sandy soils.

Extractive method		Classification[1]			Dissolving		
Extracting agent		Water	Water	Water	Water	Water	Organic solvent[2]
Additives		-	Base	Detergents	Acid	Complexing agents	-
Contaminant							
Aliphatic and aromatic hydrocarbons	volatile[3]	+/0	+/0	+/0	-	-	+
	non-volatile	0	0	+/0	-	-	+
Polynuclear aromatics		0	+/0	+/0	-	-	+
Halogenated hydrocarbons (volatile)[3]		+/0	+/0	+/0	-	-	+
Organic pesticides		+/0	+/0	+/0	0	0	+
Heavy metals and metalloids	cationic	+/0?	0	0	+	+/0	-
	anionic	0 ?	+/0	-	0	0	-
cyanides	free	+	+	+	-	0	-
	complex	0	+	-	-	-	-
Miscellaneous (inorganic compounds)		+/0	+/0	+/0	+/0	0	-

1) This method comprises a separation of humus and fine mineral particles (approx. < 50 µm) from the soil; these compounds will end up in the residual sludge.
2) In the case of a water immiscible liquid, extraction must be preceded by the drying of the soil.
3) These will evaporate to some extent during drying and/or extraction.

Legend to the table

+	generally applicable.
+/0	occasionally applicable, depending on the actual contaminant(s) and the form in which they are present in soil.
0	seldom applicable; only a minor or moderate amount of the contaminant(s) will be removed.
-	generally not applicable.

Table 2. Survey of some relevant factors for the selection of extractive methods to treat excavated sandy soil.

Extractive method[1]	Amount of residual sludge	Demand for chemicals	Estimated costs[2] (Dfl./ tonne
Classification:			
. water (plain)	large	low	80-150[4]
. base	large	moderate	120-200[4]
. detergent	moderate/large	moderate	150-250
Dissolving:			
. acid	small/moderate	high	150-300
. complexing agent	small/moderate	high	> 200
. organic solvent	small	3)	> 200

1) see also table 1.
2) Dfl. 1.00 approx. US $ 0.40 (January 1987).
3) depending on the recovery rate of the used solvent.
4) actual prices of operational installations.

OPERATIONAL INSTALLATIONS FOR EXTRACTIVE TREATMENT

Heijmans Milieutechniek B.V.

Heijmans' installation for extractive cleaning (5) has been in operation since the spring of 1985. Its capacity is up to 10-15 tonnes of soil per hour. The entire installation has been constructed in containers and is therefore transportable. A simplified process scheme of the installation is given in figure 1.

Generally the cleaned extracting agent is recirculated as much as possible. pH May be controlled between approx. 3 and 12 in almost every apparatus of the plant.
The firm claims the following potential fields of application:
- Cyanides;
- Water immiscible and low-density hydrocarbons (<1000 kg/m^3);
- Heavy metals;

or combinations of these types of contaminant (see also table 1). The soil should contain less than 30% of fine solids (< 63 μm) and humuslike compounds.
Table 3 gives some examples of practical experience obtained so far.

HWZ Bodemsanering BV

HWZ has developed an extractive cleaning plant (6) for sandy soil in cooperation with TNO (Dutch Organization for Applied Scientific Research). The plant has a capacity of 20 tonnes of soil per hour and has been in operation since the fall of 1984. A simplified process scheme is given in figure 2.

The plant was initially developed for the cleaning of soil contaminated with cyanides. Besides cyanides, the potential applicability of the installation is conformable to table 1. Thus the installation may be considered for cleaning soil contaminated with mineral oils, aromatics, PNA's, some chlorinated hydrocarbons, cyanides and/or heavy metals. Some of the results obtained so far are given in table 4.

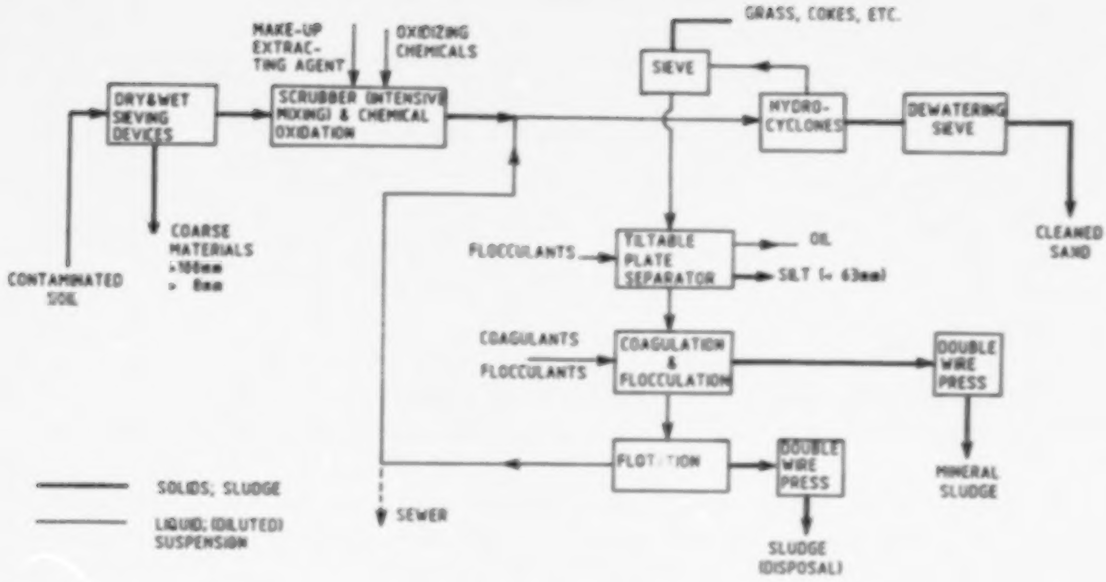

MAKE-UP EXTRACTING AGENT
OXIDIZING CHEMICALS
GRASS, COKES, ETC.
DRY&WET SIEVING DEVICES
SCRUBBER (INTENSIVE MIXING) & CHEMICAL OXIDATION
SIEVE
HYDRO-CYCLONES
DEWATERING SIEVE
COARSE MATERIALS >100mm > 8mm
CONTAMINATED SOIL
CLEANED SAND
FLOCCULANTS
TILTABLE PLATE SEPARATOR
OIL
SILT (< 63µm)
COAGULANTS
FLOCCULANTS
COAGULATION & FLOCCULATION
DOUBLE WIRE PRESS
MINERAL SLUDGE
SOLIDS; SLUDGE
LIQUID; (DILUTED) SUSPENSION
SEWER
FLOTATION
DOUBLE WIRE PRESS
SLUDGE (DISPOSAL)

Fig. 1. Process scheme of the installation of Heijmans Milieutechniek B.V.

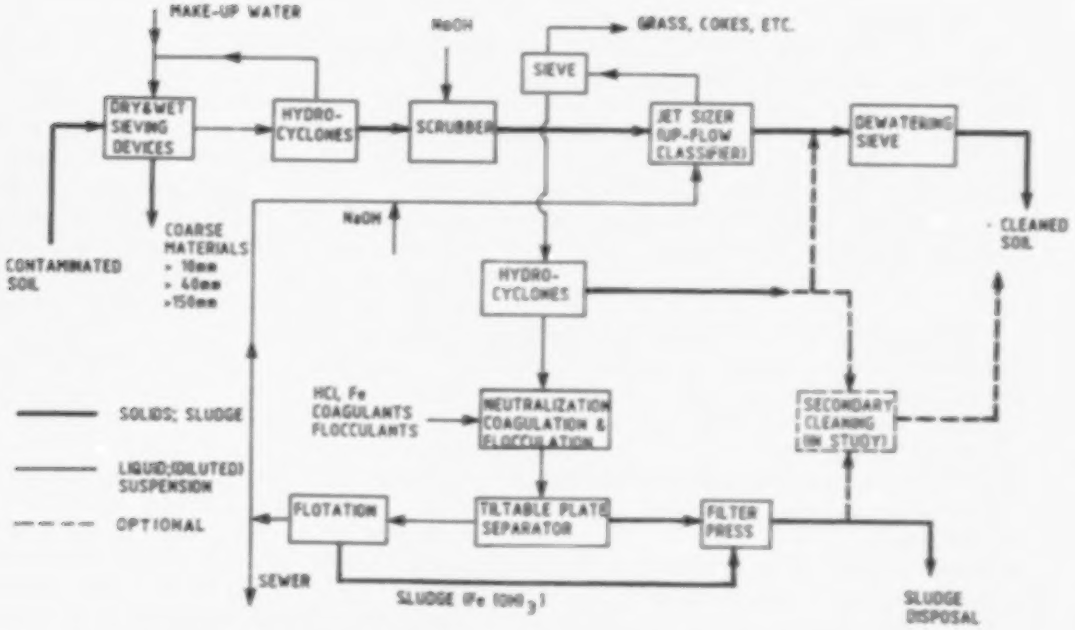

MAKE-UP WATER
NaOH
GRASS, COKES, ETC.
SIEVE
DRY&WET SIEVING DEVICES
HYDRO-CYCLONES
SCRUBBER
JET SIZER (UP-FLOW CLASSIFIER)
DEWATERING SIEVE
NaOH
CLEANED SOIL
COARSE MATERIALS > 10mm > 40mm >150mm
CONTAMINATED SOIL
HYDRO-CYCLONES
HCl, Fe COAGULANTS FLOCCULANTS
NEUTRALIZATION COAGULATION & FLOCCULATION
SECONDARY CLEANING (IN STUDY)
SOLIDS; SLUDGE
LIQUID;(DILUTED) SUSPENSION
OPTIONAL
FLOTATION
TILTABLE PLATE SEPARATOR
FILTER PRESS
SEWER
SLUDGE (Fe (OH)3)
SLUDGE DISPOSAL

Fig. 2. Process scheme of the installation of HWZ Bodemsanering B.V.

Table 3. Some results of test runs carried out with the extractive installation of Heijmans.

Contaminant	Initial concentration (mg/kg)	Concentration after treatment (mg/kg)	Removal efficiency (%)
mineral oil	3.000-8.000	90-120	appr. 98
galvanic CN	450	15	appr. 97
Zn	1.600-3.200	300-500	appr. 83
Cd	66- 125	5- 10	appr. 92
Ni	250- 890	85- 95	66-89

Table 4: Some practical experiences with the extractive installation of HWZ.

Contaminant	Initial concentration (mg/kg)	Concentration after treatment (mg/kg)	Removal efficiency (%)
CN (gaswork)	100-200	approx. 10	approx. 95
PNA (gaswork)	160-190	0,4-17	90-99
EOCL	20-24	0,3-0,5	98-99
Zn	81	27	67
Pb	approx. 10	approx. 25	approx. 75

Bodemsanering Nederland B.V.

The installation of Bodemsanering Nederland (BSN) has been in operation since 1983 and was originally developed to separate oil from sandy soil. Its capacity is approximately 20 t/h, and the installation can easily be transported to a contaminated site (7).

The oil separation is based on a high pressure water jet curtain spouting loose the contaminants from the sand particles. A simplified process scheme is given in figure 3. The process usually uses water without any additives. This fact offers the option of an additional microbiological treatment of the spent process water and/or the treated sand, as has been indicated in the process scheme. Often the process water will be largely or completely recirculated to the high pressure separator.

BSN claims the following fields of application:

- All aliphatics and aromatics with low densities (floating on water).

- Contaminants that are largely adsorped to those soil particles that will end up in the residual sludge.
- Volatile contaminants, e.g. per- and trichloro ethylene. (These are stripped to the air when the soil is led through the high pressure washer. If necessary, off gases can be treated by active carbon absorption).
- Some water-soluble and biodegradable hydrocarbons, provided the microbiological option is chosen.
- All types of soil with a maximum amount of residual sludge (< 65 µm) of approx. 20% or approx. 2.5 t/h.

Some results obtained with this installation are given in table 5.

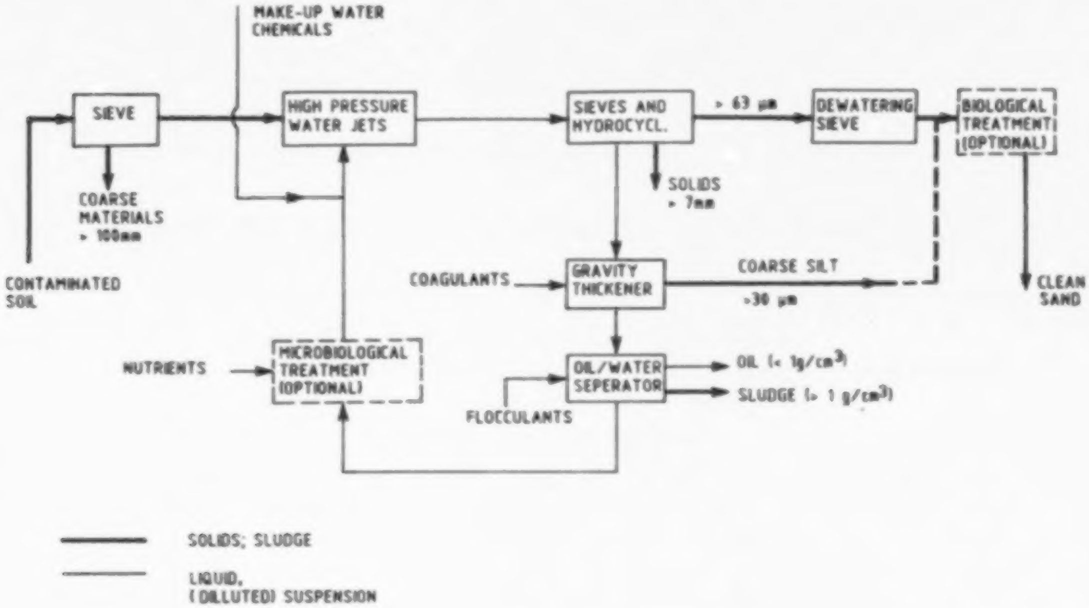

MAKE-UP WATER
CHEMICALS
SIEVE
HIGH PRESSURE WATER JETS
SIEVES AND HYDROCYCL.
> 63 µm
DEWATERING SIEVE
BIOLOGICAL TREATMENT (OPTIONAL)
COARSE MATERIALS > 100mm
SOLIDS > 7mm
CONTAMINATED SOIL
COAGULANTS
GRAVITY THICKENER
COARSE SILT
>30 µm
CLEAN SAND
NUTRIENTS
MICROBIOLOGICAL TREATMENT (OPTIONAL)
OIL/WATER SEPERATOR
OIL (< 1g/cm³)
SLUDGE (> 1 g/cm³)
FLOCCULANTS
SOLIDS; SLUDGE
LIQUID, (DILLUTED) SUSPENSION

Fig. 3. Process scheme of the installation of Bodemsanering Nederland B.V.

Table 5: Some practical experiences with the treatment installation of BSN.

Contaminant	Concentration before treatment (mg/kg)	Concentration after treatment (mg/kg)	Removal efficiency (%)
Aromatics	240	45*	81
PNA's	295	15	95
Crude oil	79.000	2.300	97

* The concentration of aromatics was reduced to 10 mg/kg due to microbiological activity 6 months after treatment.

Other operational installations and recent developments

In addition to the above examples other operational extractive installations in the Netherlands include the following:

- A so-called thermal washing installation of Ecotechniek BV. The installation has a capacity of approx. 20 tonnes per hour and is especially suitable for sand heavily contaminated with (crude) oil, preferably less dense than water.
- Two froth flotation units of Heidemij Milieutechniek BV and Mosmans Mineraaltechniek B.V. These installations have a capacity of 30 and 15 tonnes per hour respectively and are basically suitable for removing all types of contaminants. The treatment results are comparable to or sometimes even better than those of classification-based methods.
- IMU B.V. has developed a treatment method whereby an extractive step is followed by a thermal treatment step. A pilot plant with a capacity of 15 tonnes a hour is operational; it is applicable to virtually all types of contaminants.

Research is still going on to improve existing installations and to increase the applicability of extractive methods in general. In particular much effort is given to heavy metal contaminations and problems related to residual sludges.

CONCLUSIONS

- Extractive methods comprise a number of techniques, with the common feature that the contaminants in the soil are transferred to a suitable liquid.
- In principle, all types of contaminants may be largely removed from soil by extraction, if only the right process and process conditions are chosen.
- Extractive methods are especially suitable for sandy soil, because the slow and non-settling particles (clay and silt <30....60 µm; humus) will generally end up in a contaminated residual sludge. Generally this sludge has to be disposed of. Moreover, clay particles and humus are much more difficult to clean than sand particles.
- Up to now, at least 6 installations for extractive cleaning of excavated soil are operational in the Netherlands. There is a partial overlap in as far as the specific applicabilities of these installations are concerned, since they are all based on aqueous extraction agents. The annual capacity of these installations is approx. 200,000 tonnes.
- The operational installations have proven to be applicable for cyanides, PNA's and mineral oil; heavy metals, halogenated hydrocarbons and other contaminants are often also removed to a great extent (> 80%).

LITERATURE

1. W.H. Rulkens, J.W. Assink: Extraction as a method for cleaning contaminated soil: possibilities, problems and research; Proc. Conf. Management. Uncontrolled Hazardous Waste Sites, Washington DC 1984 (Hazardous Materials Control Research Institute, Silver Spring, Maryland, 1984) pp 576-583.
2. M.A. Smith (edit.): Contaminated Land: Reclamation and Treatment. Plenum Press, New York and London, 1985.
3. Handboek Bodemsaneringstechnieken (Handbook Techniques for Remedial Action), Staatsuitgeverij, The Hague, 1983.
4. J.W. Assink: Extractive methods for soil decontamination; a general survey and review of operational treatment installations in Contaminated Soil; J.W. Assink, W.J. van den Brink (eds.); Martinus Nijhoff Publishers, Dordrecht, 1986.

5. Personal communication with B. Hilberts (Heijmans Milieutechniek B.V., P.O. Box 2, 5240 BB Rosmalen, Netherlands).
6. Personal communication with C.J. Muntinga (HWZ Bodemsanering B.V., Vanadiumweg 5, 3812 PX Amersfoort, Netherlands).
7. Personal communication with G.H.J. Ruiters (Bodemsanering Nederland B.V., P.O. box 22002, 6360 AA Nuth, Netherlands).

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

EVALUATING ELECTRO-KINETICS AS A REMEDIAL ACTION TECHNIQUE

Jao-Jia Horng and Sunirmal Banerjee, Ph. D
Department of Civil Engineering
University of Washington
Seattle, Washington 98195

and

Jonathan G. Herrmann
Hazardous Waste Engineering Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

The use of electro-kinetics has found successful field application in dewatering of ground and to a limited extent in reclamation of naturally contaminated soils. The objective of the project described in this paper is to evaluate the likely operational success of the technique in decontaminating soils at a Superfund site. The evaluation is being carried out by conducting both laboratory experiments at the University of Washington and field experiments at the United Chrome Products, Inc. (United Chrome) Superfund site near Corvallis, Oregon. These experiments will address the consequences of placing a direct current (d.c) electrical field across contaminated soils in order to enhance the migration of pollutants from the soil to a point of collection. The information presented in this paper describes the laboratory testing apparatus and the laboratory experiments that have been performed on samples of the contaminated soil taken from the United Chrome site. Results of the laboratory experiments are presented along with conclusions on the potential effectiveness of electro-kinetics treatment at United Chrome.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

The Superfund Amendments and Reauthorization Act of 1986 (SARA) has placed increasing emphasis on the development of innovative technologies to manage hazardous wastes at Superfund sites. This emphasis has superceded the concept of relying on land-based containment technologies which essentially do little to reduce the overall hazardous nature of the contained wastes. Due to this changing emphasis, the U. S. Environmental Protection Agency's (EPA's) base Superfund research program is evaluating those technologies which are just emerging as possible remedial action techniques at Superfund sites. (6) The evaluation of electro-kinetics has been assigned to this latter category since the basic processes that determine the effectiveness of electro-kinetics treatment are not well understood. Also, there appears be limited interest at this time by the private sector in developing electro-kinetics treatment to a point where it could be evaluated on a pilot or field-scale basis.

Over the past decades, evidence has been gathered to show that when subjected to electro-kinetics treatment, the physico-chemical characteristics of a saturated soil deposit can undergo permanent changes. These changes in the characteristics of soil deposits are due to a variety of processes, (e.g., movement of water, ion migration and diffusion, ion exchange, mineral decomposition, precipitation of secondary minerals, electrolysis, hydrolysis, oxidation and reduction of ionic species, and heat and gas generation). Many previous studies (2,3,4,5) have indicated that from a technical viewpoint electro-kinetics treatment may be a feasible approach for decontaminating polluted soils. This is based, however, on the fact that the hydrogeologic system is amenable to the constraints of electro-kinetics treatment as it is presently understood.

PURPOSE

The purpose of the research described here was to:

a) conduct a series of experiments with systematic variation of hydraulic and electo-kinetic variables (e.g., hydraulic gradient, induced flow velocity, total flow velocity, total fluid flow, strength and direction of electric field, treatment time interval and total current) which can influence the electro-kinetics treatment of soil and,

b) evaluate the effects of treatment in terms of changes in concentration of metal ions (i.e., chromium).

With some understanding of the effectiveness of electro-kinetics treatment in the laboratory, a pilot-scale test at the United Chrome site could be properly designed.

APPROACH

Site Selection

A review of information on the United Chrome site indicated that it was a candidate for electro-kinetics treatment. The site covers approximately 0.6 hectares (ha) of level ground. The site is neither so large that a relatively untested technique might be considered too risky for the benefits expected, nor it is so small that excavation and disposal of the contaminated soil at a hazardous waste disposal facility might be considered desirable. The hydrogeologic conditions at the site and the hydraulic conductivity of the subsurface soils are also suitable for electro-kinetics treatment. The groundwater table at the site varies from between 0 to 13 meters (m) in depth depending upon the season. During wet winters, the water table is located at 0 to 2.5 centimeters (cm) below ground surface. Furthermore, there is very little flow of groundwater through the site and the average hydraulic gradient of the site is approximately 0.008 m/m. The contaminated near-surface soils are adequately permeable for electro-kinetics treatment since the data indicate that the hydraulic conductivity may range from 5×10^{-4} cm/sec (1) to 5×10^{-6} cm/ sec. (current investigation). All of these characteristics, (e.g., appropriate areal extent of the site, nearly static groundwater regime, and saturated moderately permeable soils at shallow depth) are suitable for hydraulic leaching and electro-kinetics treatment of the soils at United Chrome.

The relatively simple chemistry of the wastes at the United Chrome also favors in-situ treatment. The contaminants at the site are inorganics which exist in the soil-water system as cations and anions. The most important of these contaminants is hexavalent chromium (CrVI) which exists in anionic form as CrO_4^{-2} or $HCrO_4^-$ or $Cr_2O_7^{-2}$ depending upon the pH and concentration of the chromium ion in the soil-water system. The removal of anionic chromium or chromate appears to be the major target for any in-situ treatment effort at the site. Chromate is relatively unreactive with soils and is not expected to be significantly retarded in its migration by adsorption or precipitation. Further, chromate is present at a concentration in the range of 100 - 10,000 mg/l and is a major ionic constituent of the solution. (1) Hence, it can be transported by ionic migration with relatively high efficiency and with relatively low electrical power consumption.

Field Exploration

Three shallow borings were made at United Chrome with 15-cm hollow stem augers for the purpose of retrieving soil samples for the laboratory studies. One of the borings was located near a dry well and a second was located at the entrance to the property since both of these locations were the areas where near-surface soils were substantially contaminated. Two shallow wells with stainless steel casings and screens were installed in the borings. A third boring was made east of the United Chrome building in order to obtain samples of uncontaminated soils located outside the contaminant plume. Cores from the three borings were obtained using stainless steel Shelby tubes 6.3 cm in diameter.

Testing Program and Methodology

An outline of the hydraulic leaching and electro-kinetics treatment experiments are presented in Table 1. In order to minimize the disturbance of the sample to be tested a 5-cm diameter thin-wall tube was inserted into the aforementioned Shelby tube. The soil sample in this thin-walled tube was transferred to a plexiglass oedometer (see Figure 1). The oedometer was specifically designed and built for performing laboratory electro-kinetics tests. The oedometer is a 5-cm (inside diameter) plexiglass cell with electrode assemblies at both ends. Each electrode assembly

Table 1. Hydraulic and Electro-kinetic Leaching Experiments 1 through 8 with Contaminted Soils Using the Oedometer

Experiment No.	Description of Testing
1	The leaching of chromium from the soil column was first tested by flushing with tap water at 0.14 kg/cm² hydraulic pressure. Several short-duration applications of electrical field were also made on this sample to obtain the electro-osmotic conductivity.
2	Several hydraulic pressures were employed in leaching the chromium from the soil column.
3	The effects of different combinations of electrical field and hydraulic leaching were tested in order to study the effect of these changes on the chromium removal.
4	The effects of different strengths and directions of hydraulic and electro-kinetic fields on chromium removal were examined.
5	The soil column was changed from vertical to horizontal position in Experiments 5 through 8. The effluent of the oedometer was withdrawn at the anode during application of constant hydraulic pressure (0.28 kg/cm²) and constant electrical field (1.0 V/cm).
6	Initially, the effluent was withdrawn at the cathode during the simultaneous treatment with a constant electrical field (1.0V/cm) and a hydraulic pressure (0.07 or 0.14 kg/cm²). Then the electrical field was reversed twice in order to study the effect on chromium removal.
7	The influence of a lower electrical field (0.1 V/cm) on chromium removal was investigated under simultaneous hydraulic and electro-kinetic treatment with the fluid effluent at the anode.
8	Electrical fields of 0.25 V/cm to 0.1 V/cm with a hydraulic gradient were tested to study the effect on chromium removal. The effluent was collected at the anode.

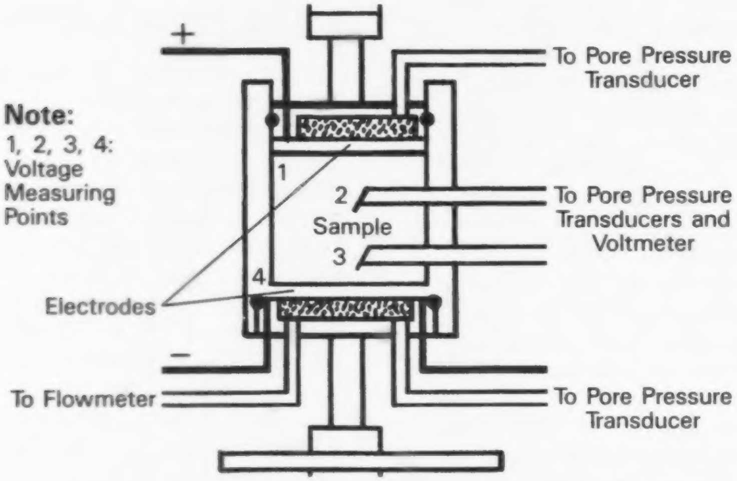
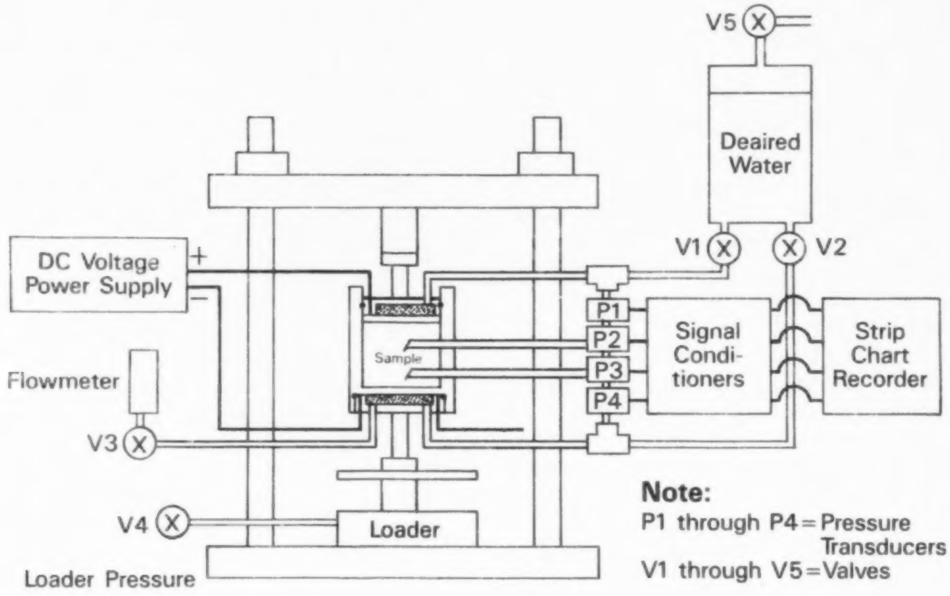

+
To Pore Pressure Transducer
Note:
1, 2, 3, 4: Voltage Measuring Points
1
2
Sample
3
4
To Pore Pressure Transducers and Voltmeter
Electrodes
−
To Flowmeter
To Pore Pressure Transducer

Figure 1: Laboratory Electro-osmotic Oedometer

consists of a nickel-copper wire-mesh electrode, mounted on top of a porous stone. The electrode assembly, at the top end, can move in relation to the cell to accomodate the consolidation processs within the soil sample. During an experiment, pore water pressure is monitored by a pore pressure transducer which is in hydraulic connection with a closed electrode. Also, flow rate measurements across the cathode can be made from a variable area flowmeter connected to another hydraulic line at the cathode. Two stainless steel hypodermic needles can be inserted into the soil sample at the distances of 1.2 and 3.7 cm from the cathode so that measurements of pore pressure and electrical potential at certain locations in the sample may be made. A piece of plastic tubing is fitted around the outside wall of the needle in such a manner that the measured voltage reflects the potential of the soil around the tip. A diagrammatic drawing of the test set-up for an electro-osmotic test is presented in Figure 2. The set-up consists of the previously described oedometer, a loader, a DC power supply, a variable area flowmeter, a de-aired water tank connected to a pressure source, pore water pressure transducers, signal conditioners, and a strip chart recorder. After the soil sample is placed into the oedometer both ends of the oedometer are mounted with the wire-mesh electrodes, filter papers, and porous stones. De-aired tap water is introduced from a tank by compressed air to the bottom of the oedometer to saturate the soil sample. Following saturation, the



Note:
P1 through P4 = Pressure Transducers
V1 through V5 = Valves

Figure 2: Schematic Arrangement for Laboratory Testing

oedomter is fixed either vertically (Experiments 1 through 4) or horizontally (Experiments 5 to 8). Horizontal orientation of the cell is always considered preferable since reversal of polarity of the electrodes does not introduce electrokinetic flow against gravity.

RESULTS

Data Evaluation

To develop an appropriate treatment approach by combining hydraulic leaching and electro-kinetics treatment, it is necessary to examine their interactions. In the series of experiments, briefly described in Figure 1 the removal of chromium was first tested by hydraulic leaching only (Experiments 1 & 2). In the subsequent experiments an electrical potential was imposed on the hydraulic flow to study its influence on chromium removal. Results from the experiments have been presented as normalized curves (Figures 3 through 6) showing the cumulative fraction of chromium removed versus the cumulative volume of water removed(in units of soil column volumes).

Some general observations about the experiments are appropriate now. Most of the chromium (over 99%) leached from the soil is soluble hexavalent chromium (Cr VI) in the anionic forms of CrO_4^{-2}, $HCrO_4^-$ or $Cr_2O_7^{-2}$ rather than the fairly insoluble trivalent chromium (Cr III) cation. However, the value of chromium concentration was reported as total chromium in the experimental results in accordance to the analysis method. Chromate species are the dominant anions; therefore a significant fraction of the electrical current should be carried by the chromium ions. The experiments were generally carried out over time periods of a week to two weeks. During the course of an experiment at constant voltage and/or constant hydraulic pressure, the electrical current flow and/or the hydraulic flow tended to decrease moderately. The internal decrease in hydraulic conductivity and increase in electrical resistance may be experimental artifacts of the oedometer test cell. The evaluation of these parameters and their change during testing is a major objective of the proposed field work.

The chromium removal by hydraulic leaching of the soil column appeared to depend only on the total water flow through the soil column and was apparently independent of the hydraulic pressure applied on the soil column. Though Experiments 1 & 2 were tested under different hydraulic pressures, no significant difference in the ratios of total leached chromium was observed (Figure 3). It can be seen that chromium removal increased so that more than half was removed with a volume ratio (volume of fluid collected to volume of soil column) of 0.5, which corresponds approximately to one pore volume of water passing through the soil column. Chromium removal was substantially complete with a volume ratio of 1 to 1.2. These results indicate that there was some dispersion of contaminants during hydraulic leaching, but that the retardation of chromium was very slight. The results in Figure 3 were combined and used as a comparison for the electro-kinetic effect on the removal of chromium from the soil column in subsequent experiments. (Experiments 3 through 8).

The imposition of an electrical field along with hydraulic leaching

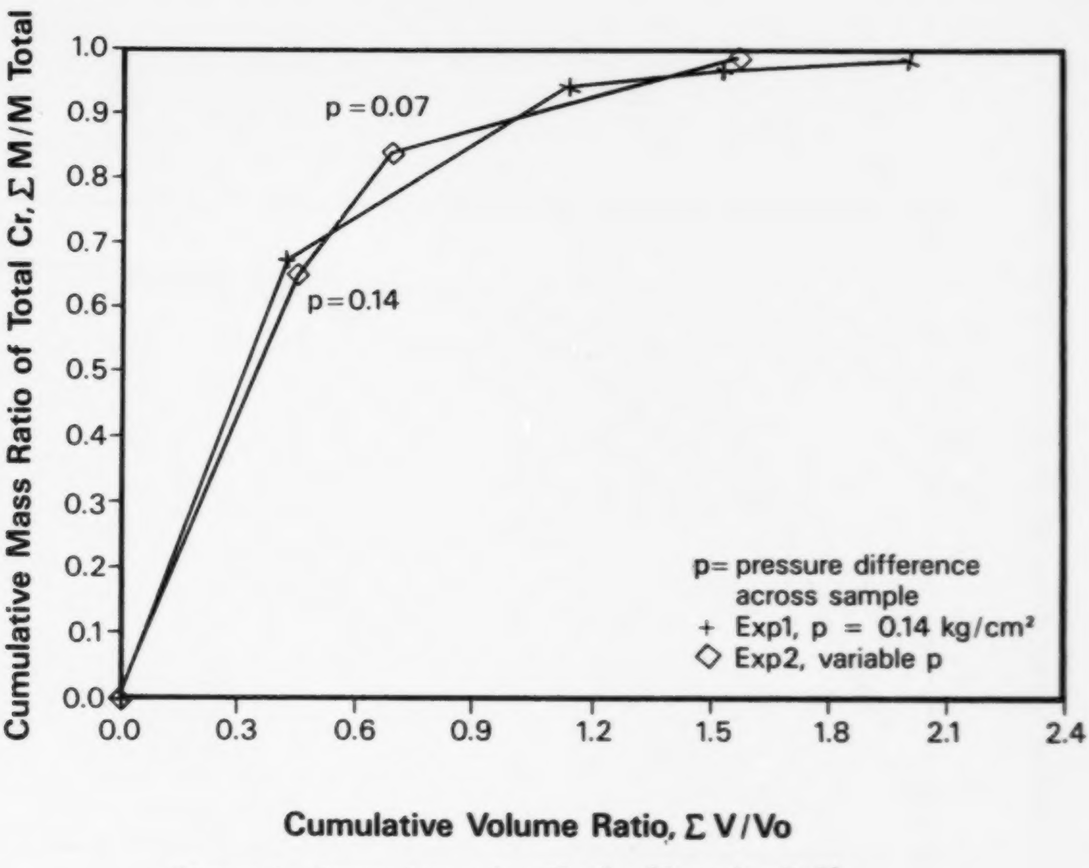


Figure 3: Comparison of a Single (Experiment 1)
Versus a Variable (Experiment 2)
Hydraulic Pressure.

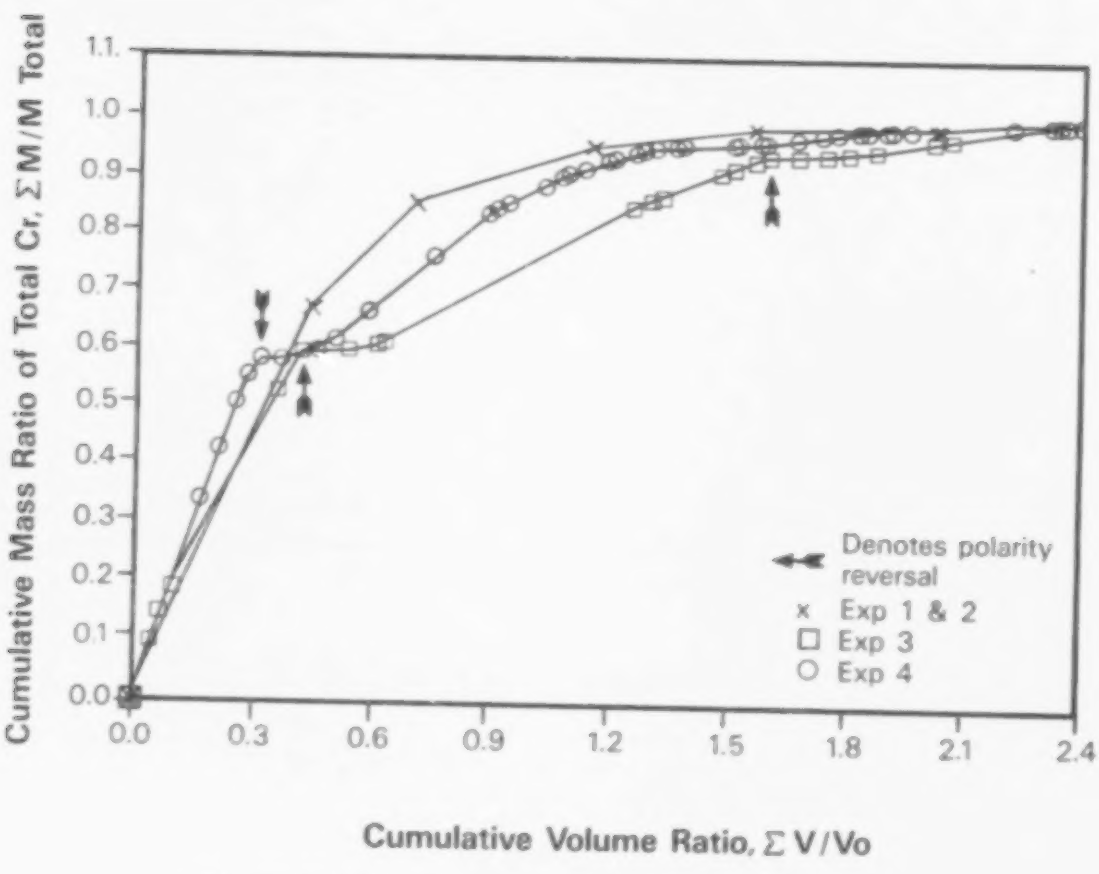


Figure 4: Comparison of Combined Hydraulic Pressures (Experiments 1 & 2) Versus Combined Hydraulic Pressures and Electric Field (Experiment 3) Versus Combined Hydraulic Pressures and Electric Field with Polarity Reversal (Experiment 4).

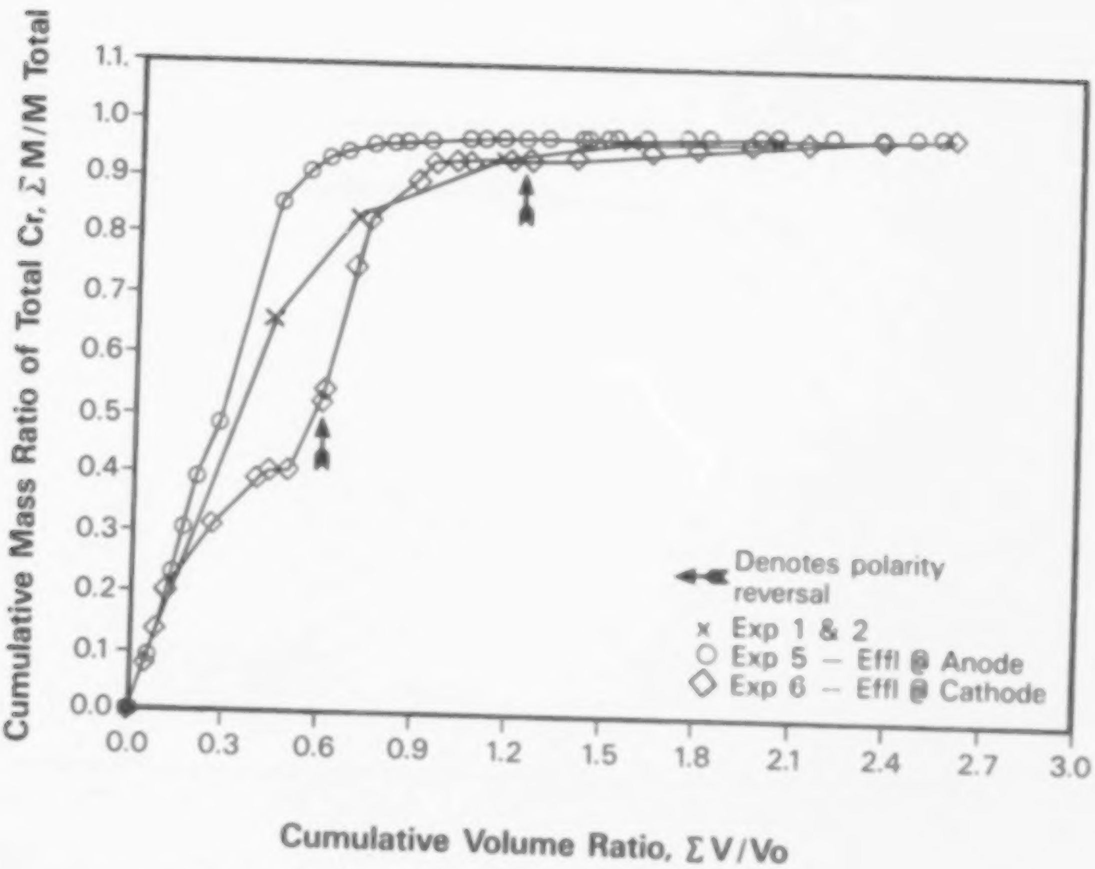


Figure 5: Comparison of Combined Hydraulic Pressures (Experiments 1 & 2) Versus Effluent Removal at the Anode (Experiment 5) Versus Effluent Removal at the Cathode (Experiment 6).

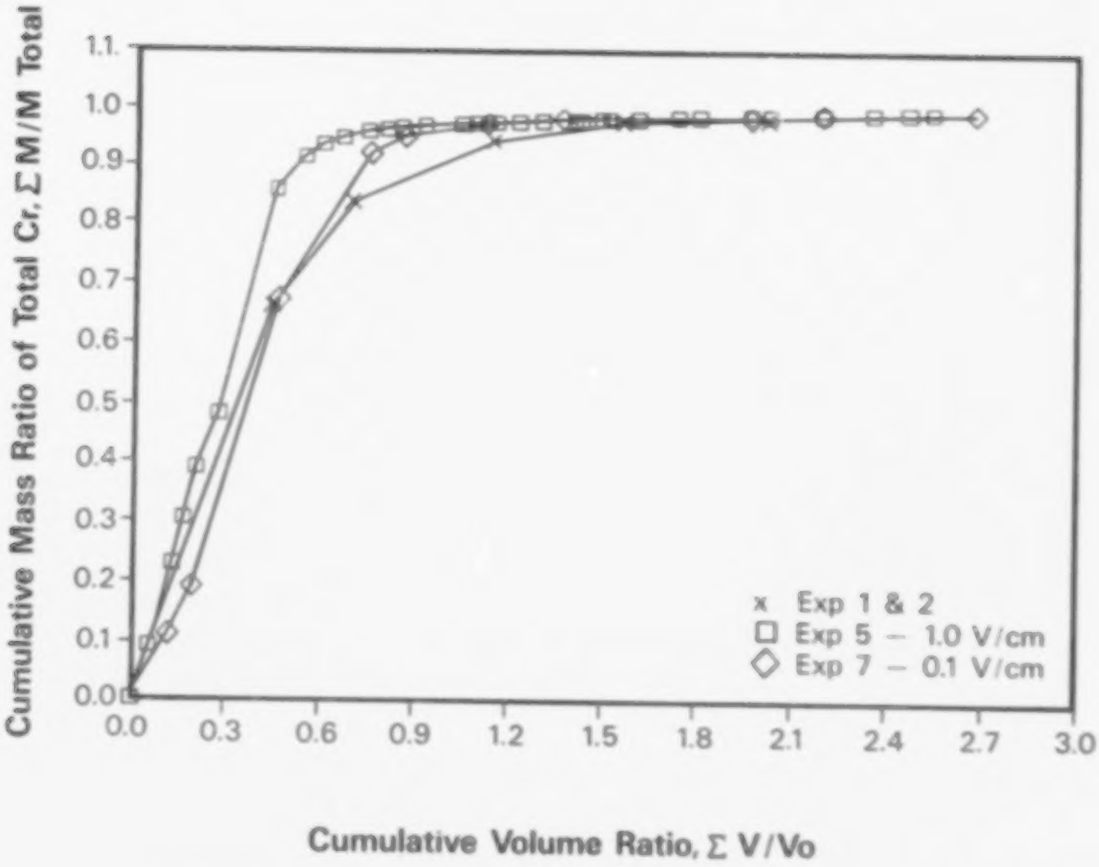


Figure 6: Comparison of Combined Hydraulic Pressures (Experiments 1 & 2) Versus Two Voltages (Experiments 5 & 7) at a Constant Hydraulic Pressure.

of the soil columns either reduced (Experiments 3, 4 and 6) or enhanced (Experiment 5) removal of chromium, as shown in Figures 4 and 5. In Figure 4 (Experiments 3 and 4), chromium removal was retarded, primarily due to reversing the direction of net fluid flow. More water was required to flow through the column in order to achieve the same chromium removal as in Experiments 1 & 2. In these early experiments, it was thought that relatively frequent reversals of flow direction or electric field would yield useful experimental information. However, a delayed response in the chromium concentration was noted due to a dead volume of fluid in the tubing and porous stones. The delayed response was observed in both Experiments 3 and 4. It was recognized as an unavoidable experimental problem that could be reduced by minimizing changes in flow direction and by using longer experimental testing times.

Several observations can also be made regarding the basic electrokinetic process. When electrokinetics was the only treatment, an increase in the pH of the water sample collected from the cathodic effluent was observed after the delay mentioned previously. In addition, gases evolved and accumulated at the cathode. The pH increase and gas production at the cathode implies the electrolysis of water, which is a likely cathode reaction. This pH change may also cause secondary chemical reactions. The produced gases and drying caused by heat that is generated may increase the electrical resistance and decrease the efficiency of electrokinetics treatment. Chloride ions behaved most similarly to the chromate; however, all anions tended to change concentration simutaneously.

The concentration changes of cations (sodium and calcium) were similar to the concentration changes of chromium in the leached water sample of Experiment 4. Since chloride and sodium ions are unlikely to react chemically with soil, thereby retarding their leaching, the similar behavior of chromate ions to both of them suggests that displacement of pore water was the most important mechanism for removing chromium in Experiments 3 and 4 and that the effect of electro-kinetics was relatively small. It was shown in Experiments 5 and 6 (Figure 5) that electro-kinetics treatment combined with hydraulic leaching can have a great influence on the removal of chromium from the United Chrome soils. In particular the selection of the anode or cathode for withdrawal of effluent exerts a dramatic effect on chromium removal. By withdrawing the column effluent from the anode Experiment 5 achieved a more successful removal of chromium than was achieved in Experiments 1 & 2.

A gradual decrease of chromium removal in the initial stage of Experiment 6 (as shown in Figure 5) was due to the collection of water at the cathode. After this decrease of chromium removal in Experiment 6 was noted the polarity of the electrical field was reversed, which changed the water collection to the anode, and chromium removal increased rapidly (slope increase as seen in Figure 5). When another reversal of electrical field was made to change the water collection back to the cathode, a decrease in slope was again noted, but the effect was small because most of the chromium had already been flushed out of the soil column. These results suggest that effluent for chromate removal should be collected at the anode. The results also suggest that reversing the electrical field should be avoided during the combination of hydraulic leaching and electro-kinetics treatment because withdrawal of the fluid from the cathode always depresses the chromium removal.

The effect of the electrical field strength during the combined treatment was examined in Experiments 5 and 7. Effluent was collected at the anode in both of these tests. Experiments 5 and 7 were more successful in removing chromium from the soil column than Experiments 1 & 2 (Figure 6). To achieve a 95% removal of chromium, Experiments 1 & 2, 5, and 7 would require about 1.1, 0.5, and 0.8 soil volumes of water, respectively. These results indicate that electrokinetics treatment may significantly reduce the time of in-situ treatment as well as the volume of contaminated water that must be treated once it is removed from the ground. No significant difference in the cummulative removal of total chromium was observed in the very early stages of treatment (Figures 5 and 6) regardless of the direction and strength of the electrical field vis-a-vis the direction of the hydraulic leaching. The beneficial effect of electro-kinetics in these experiments only became apparent when the volume ratios (volume of fluid collected to volume of soil column) was about 0.3 (Experiment 6 in Figure 5) up to about 0.5 (Experiments 5 and 7 in Figure 6). The volume ratio of 0.5 is approximately equal to the porosity of the soil column in these experiments. This fact suggests that the displacement of the pore water from the pore space in soil may play an important role in the early stage of treatment (when the water volume flow through the soil is less than 0.3 times the soil volume) whether the electric field is imposed or not. After this early stage, however a significant difference in chromium removal by combined hydraulic leaching and electro-kinetics treatment was observed.

Conclusions

The following conclusions may be drawn from the results of these experiments and applied to the United Chrome site:

(1) It appears that the combination of hydraulic leaching and electro-kinetics treatment can accelerate chromium removal compared to hydraulic leaching alone (Figure 6). This acceleration should be much more pronounced in a field test at United Chrome where the hydraulic gradient will be low relative to the electrical potential applied.

(2) The displacement of polluted pore water by hydraulic leaching dominates the early stage of chromium removal from the United Chrome soils until the water flow through the column is about one-half of the fluid to soil column ratio, (as seen in Figures 5 and 6). Sometimes, the electro-kinetic effect can be discerned as early as approximatley one-third of the fluid to soil column ratio (Experiment 6 in Figure 5).

(3) The choice of the anode for collection of effluent during simultaneous hydraulic leaching and electro-kinetics treatment determines the success of accelerating chromium removal from the United Chrome soils as shown in Figure 5. When

the cathode was chosen, chromium removal was depressed. When the effluent was collected at the anode, increased chromium leaching was observed. There is no advantage to reversals of either the electrical field or hydraulic flow during the combined treatment.

(4) The possible mechanisms involved in the combination of both hydraulic leaching and electrokinetics treatment are dispersion due to the hydraulic flow, ion migration, water electrolysis, adsorption/desporption, and chromium reduction due to the imposed electrical field. There are significant experimental and theoretical problems in quantitatively assessing these factors and their interaction.

(5) Laboratory studies should evolve to extend the range of physical and chemical conditions studied. While laboratory studies to date have indicated the possible application of electro-kinetics to contaminated soils at the United Chrome site, considerable work is still needed to develop general guidelines for use of electrokinetics treatment.

ACKNOWLEDGEMENTS

The research described in this paper has been funded wholly or in part by the United States Environmental Protection Agency through Cooperative Agreement No. CR 811762 to the University of Washington. It has been subjected to Agency review and approved for publication, but does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The authors wish to thank Mrs. Margaret Kopriwa for clerical support in the preparation of this paper.

REFERENCES

1. CH$_2$M Hill, 1985, "Remedial Investigation Report - United Chrome Products Site Corvallis, Oregon, USEPA 106.0L32.0," Contract No. 68-01-6692, Seattle, Washington.
2. Gibbs, H.J., 1966, "Research on Electro-reclamation of Saline-Alkali Soils," Trans. ASCE, Vol. 9, p. 164-169.
3. Hamnet, R., 1980, "A Study of the Processes Involved in the Electro-reclamation of Contaminated Soils," M.S.C. Thesis, University of Manchester, U.K.
4. Puri, A.N. and Anand, B., 1936, "Reclamation of Alkali Soils by Electro-dialysis," Soil Science, Vol. 42, p. 2327.
5. Segall, B.A., O'Bannon, C.E.and Matthias, J.A., 1980, "Electro-osmosis Chemistry of Water Quality," J. of Geotechnical Division, ASCE, Vol.106, GT10, Oct. 1980, p. 1148-1152.
6. USEPA, 1986 "Superfund Innovative Technology Evaluation (SITE) Strategy and Program Plan," EPA/540/G-86/001, Washington, D.C.

OFFSITE TREATMENT OF RCRA HAZARDOUS WASTES - A CASE STUDY

Ronald J. Turner
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

ABSTRACT

The U.S. EPA's Hazardous Waste Engineering Research Laboratory has conducted sampling and analysis to evaluate solid, liquid, and air emissions at a number of commercial and industrial hazardous waste treatment facilities. The results of monitoring treatment processes at one facility are presented. The processes sampled were distillation, cyanide oxidation, metals precipitation, and a cooling tower treating contaminated ground water.

INTRODUCTION

A prohibition was promulgated for the disposal of certain listed hazardous wastes directly into or onto the land without their being treated to an acceptable degree prior to such disposal (RCRA; Hazardous and Solid Wastes Amendments of 1984). Before the U.S. Environmental Protection Agency (EPA) promulgates or codifies a hazardous waste regulation under the RCRA, data from demonstrated treatment technologies are evaluated. Waste composition and waste management information was or is being sought by the EPA for the wastes which will be subject to conditional land disposal restrictions, i.e., solvents and dioxins, "California List", and the "thirds". The solvents and dioxins rule was promulgated November 7, 1986. The promulgation date for the "California List" is July 8, 1987. Three lists of other wastes are to be evaluated by August 8, 1988, June 8, 1989, and May 8, 1990. These lists were announced in the May 31, 1985, Federal Register.

The commercial treater of wastes cooperating in this study began operations in 1970. This company owns or has interests in four facilities located in the same metropolitan area. A minor part of their operations is the treatment and recovery of waste oils for fuel blends. The two principal operations are aqueous waste treatment and solvent recycling.

Drummed wastes to be treated are tested, segregated, and stored at the main facility. Accepted wastes include acids, caustics, chlorinated organics, other organic compounds, cyanides, and metal-bearing wastes. The solvent reclamation facility also

Preceding page blank

treats cyanide wastes. The oily waste treatment operation handles bilge waters, pretreated aqueous wastes from one or more of the company's other sites, and industrial coolants.

PURPOSE

Engineering and environmental evaluations are needed to obtain operating information on existing commercial and industrial hazardous waste treatment technologies to document those which are representative of Best Demonstrated Available Technology (BDAT). This study was conducted to evaluate the processes commonly used to treat spent solvents, metal-bearing aqueous wastes, and cyanide wastes, to determine the levels of treatment achievable. Similar sampling and analysis studies will be done over the next few years for the various listed wastes and the appropriate treatment technologies at offsite waste treatment, storage, and disposal facilities (TSDF's) and at generators' facilities.

APPROACH

Commercial TSDF's accept many of the listed hazardous wastes and apply a variety of full-scale processes to the wastes to recover, detoxify, or destroy them. The EPA visited a TSDF in November 1985, to conduct a 3-day onsite sampling and subsequent laboratory analyses of waste treatment processes. The principal processes employed by the TSDF were waste solvent distillation, cyanide oxidation, and heavy-metal precipitation. Another process evaluated was the use of a cooling tower to remove volatile organic compounds from ground water. The raw waste and effluent compositions were determined by standard EPA methods.

PROBLEMS ENCOUNTERED

The electrolytic cyanide oxidation process was monitored by the EPA during the first 72 hours of the batch operation, but the actual process proceeded for approximately 192 hours. The final concentration value ($\sim$ 1000 mg/liter) was supplied by plant personnel. No solid distillation process residues were generated for evaluation during the sampling episode. The alkaline chlorination process being operated at the time of the test was not effective in reducing the cyanide concentration. The actual percent removal of heavy metals could not be determined as the materials sampled did not represent a single, discrete batch of waste. (However, the results were probably typical of the process.)

RESULTS

Aqueous Waste Treatment

This system is comprised of several unit processes arranged in series. Three basic steps are employed. First, concentrated wastes may be diluted with recycled, treated effluent; second, hexavalent chromium is reduced to trivalent with sodium metabisulfite; third, metals are precipitated with lime and settled by gravity sedimentation. After settling, the decant is pumped to a large equalization tank for testing prior to discharge to a municipal sewer. The sludge is subsequently transported offsite to a permitted facility for disposal.

Waste Solvent Distillation

Solvents are segregated based on their physical and chemical characteristics (water content, chlorine content, Btu value, flammability, etc.). Three stills are available to process the spent solvents (see Figure 1). The main still has a 500-gallon total capacity and is capable of continuous operation. During the test episode, this still was operated in a semi-batch mode at 150°F and a vacuum of 15 to 20 inches. Bottoms from this still can be either recycled, dried for disposal, or processed in one of the other two stills. The vaporized liquid solvent-water mixture is condensed and separated. The water from the main still decant and other aqueous solvent wastes from a storage tank were processed in a 1400-gallon atmospheric batch kettle operated at 212°F. The overheads from the batch kettle were processed further in a 2000-gallon batch still equipped with a packed tower.

The wastewaters remaining were chemically treated to oxidize residual organic compounds and transported to the aqueous waste treatment facility. The company's practice at this time is to ship still bottoms offsite for solidification/stabilization and disposal.

Cyanide Treatment

Treatment of cyanide wastes incorporated a two-cell electrolytic oxidation process with an alkaline chlorination process (Figure 2). The two electrolytic cells have a capacity of about 550 gallons each and operate on direct current. An air sparger provides mixing. The area above the cells is ventilated and monitored for hydrogen. The electrolytic cyanide process was designed to treat wastes containing up to 10 percent cyanide. At such concentrations, a week or more is required to oxidize the cyanides to a nominal 1000-parts-per-million concentration before completing the destruction by alkaline chlorination. The final effluent is usually combined with other aqueous wastes for further treatment at another facility.

Cooling Tower

Prior to 1970, the main plant area was owned by a paint manufacturer, and a number of solvents from spills have leached into the ground waters (Figure 3). The contamination level is about 50 parts per million of volatile organic compounds. To reduce the contaminants, the ground water is pumped from wells to a cooling tower which serves to remove heat from the recirculated plant water and to remove the volatile organic compounds. A portion of the stripped ground water is discharged to a municipal sewer.

Oily Wastewater Treatment Plant

All incoming aqueous wastes received by this facility are processed through an API separator. The effluent may be treated with potassium permanganate to oxidize phenolics and, if hexavalent chromium is present, sodium metabisulfite is added to reduce the chromium to the trivalent state. The wastewaters are then flocculated and gravity settled or centrifuged. The separated solids are shipped offsite for solar evaporation and disposal. The final effluent is sent to a municipal sewer.

ANALYTICAL PROCEDURES

The analytical procedures and reference sources are listed in the Appendix.

PERFORMANCE EVALUATIONS

Aqueous Waste Treatment

Generally, this TSDF's system was effective in treating aqueous

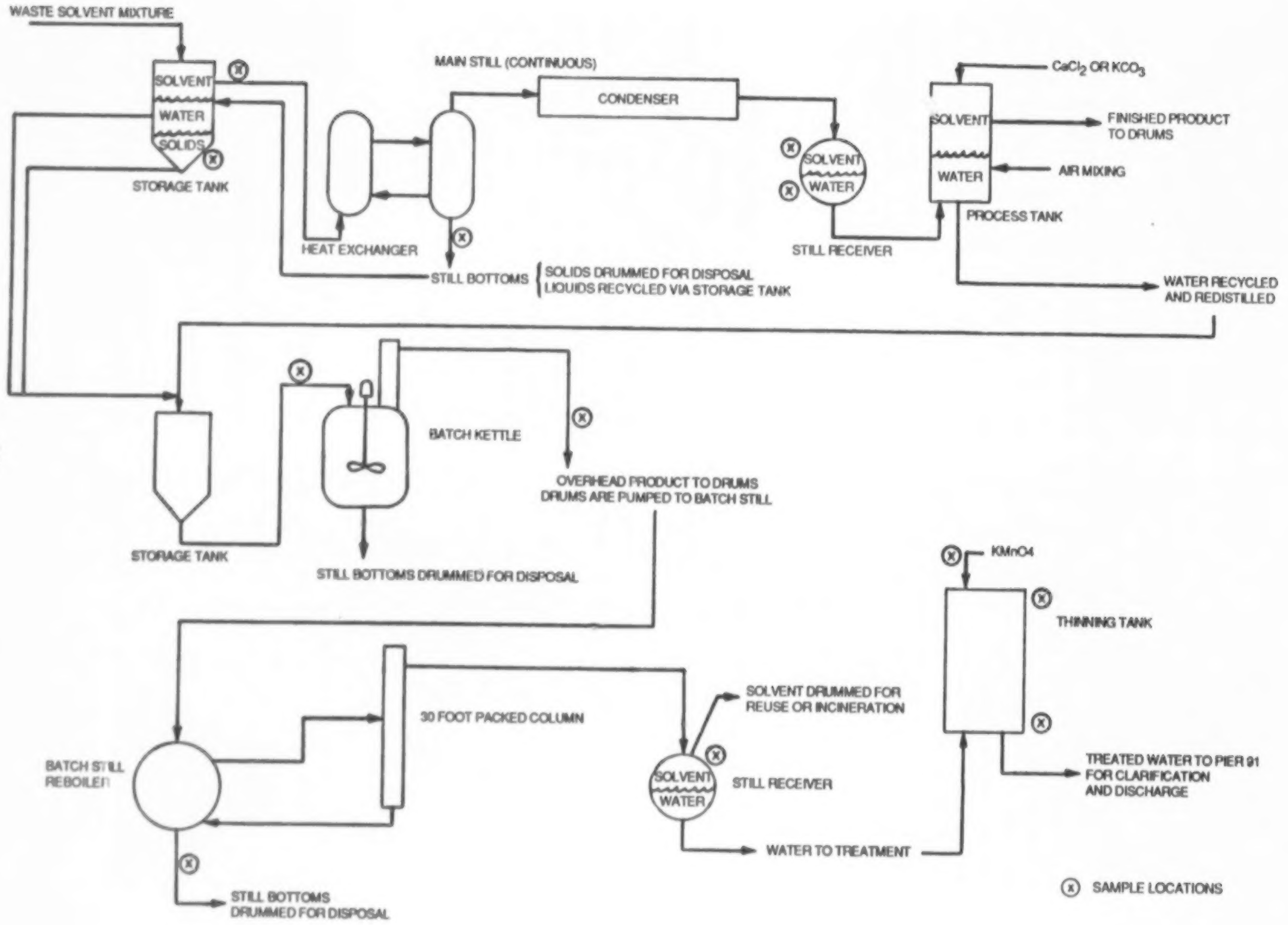

WASTE SOLVENT MIXTURE
SOLVENT
WATER
SOLIDS
STORAGE TANK
HEAT EXCHANGER
MAIN STILL (CONTINUOUS)
CONDENSER
STILL BOTTOMS
SOLIDS DRUMMED FOR DISPOSAL
LIQUIDS RECYCLED VIA STORAGE TANK
SOLVENT
WATER
STILL RECEIVER
$CaCl_2$ OR KCO_3
SOLVENT
WATER
FINISHED PRODUCT TO DRUMS
AIR MIXING
PROCESS TANK
WATER RECYCLED AND REDISTILLED
STORAGE TANK
BATCH KETTLE
STILL BOTTOMS DRUMMED FOR DISPOSAL
OVERHEAD PRODUCT TO DRUMS
DRUMS ARE PUMPED TO BATCH STILL
KMnO4
THINNING TANK
BATCH STILL REBOILER
30 FOOT PACKED COLUMN
SOLVENT
WATER
SOLVENT DRUMMED FOR REUSE OR INCINERATION
STILL RECEIVER
WATER TO TREATMENT
TREATED WATER TO PIER 91 FOR CLARIFICATION AND DISCHARGE
STILL BOTTOMS DRUMMED FOR DISPOSAL
ⓧ SAMPLE LOCATIONS

Figure 1. Distillation process.

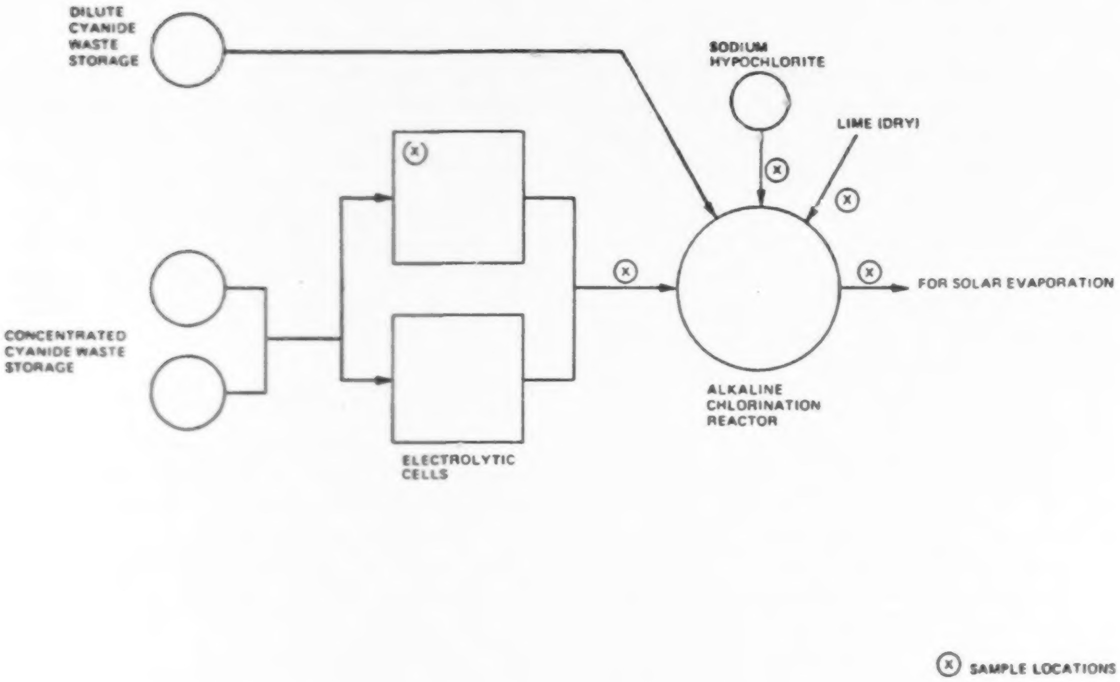

DILUTE CYANIDE WASTE STORAGE
SODIUM HYPOCHLORITE
LIME (DRY)
FOR SOLAR EVAPORATION
CONCENTRATED CYANIDE WASTE STORAGE
ALKALINE CHLORINATION REACTOR
ELECTROLYTIC CELLS
ⓧ SAMPLE LOCATIONS

Figure 2. Cyanide treatment process.

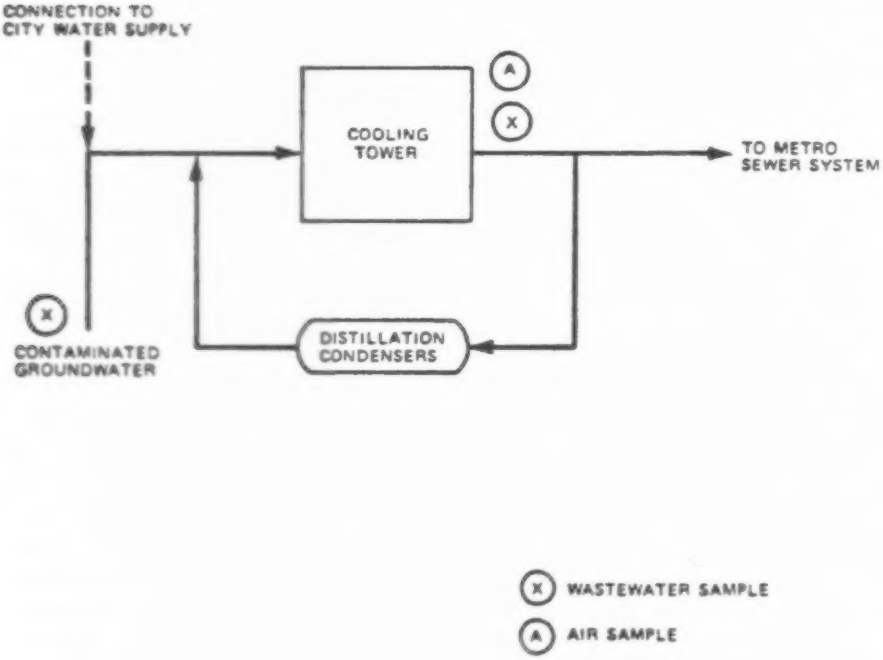

CONNECTION TO CITY WATER SUPPLY
COOLING TOWER
TO METRO SEWER SYSTEM
CONTAMINATED GROUNDWATER
DISTILLATION CONDENSERS
ⓧ WASTEWATER SAMPLE
Ⓐ AIR SAMPLE

Figure 3. Cooling tower/air stripping process.

wastes containing metals. The effluent copper and nickel concentrations, 5 and 3 milligrams per liter respectively, were higher than expected by the plant personnel. They noted that chelating agents may have been present, but this was not verified. Volatile organic compounds were detected in the influent waste samples, but the concentrations were significantly lower in the treated effluent. It should be noted that the data do not represent a single, discrete batch of waste from beginning to end. Rather, the data can be considered representative of the waste streams and the treatment processes for information purposes. The results of the tests performed on the aqueous waste samples are presented in Table 1. The gravity-thickened sludge was obtained from one of four pH adjustment/sedimentation decanter tanks. Each tank contained a treated waste from various mixed aqueous influents. The two isolation tanks contained difficult to treat wastes, i.e., chelated metals. The waste in Isolation Tank #1 was shipped offsite for treatment by solar evaporation.

At the time of the sampling, the Extraction Procedure (EP) toxicity was the only test to define hazardous waste characteristics under the RCRA. An improved method, Toxicity Characteristic Leaching Procedure (TCLP), was being developed and has subsequently been promulgated. There are some differences in the two tests. The EP toxicity provides a liquid extract which may be analyzed for eight metals, four insecticides, and two herbicides. The TCLP extracts can be analyzed for the EP toxicity parameters plus about 60 other volatile and semivolatile organic compounds. A device called a zero headspace extractor is used to leach solids for the TCLP test. The TCLP metals and volatile organic compounds are given in Table 2, together with the compositional (raw waste) and extract concentrations for the aqueous treatment operation sludge composite sample from the four decanter tanks. For example, the amount of chromium detected in the TCLP extract was 370 mg/liter.

Waste Solvent (Distillation)

The batch of waste solvent processed by the main still was predominantly methyl ethyl ketone (MEK). As illustrated in Table 3, the finished solvent product contained about 91 percent MEK. However, the condensed water layer (finished product water) and the still bottoms required further treatment because of high solvent content.

The influent to the batch kettle was the water layer from the main still together with some materials from a waste solvent storage tank. The mixing of these two streams produced a blend containing more than 25 percent organics. The overhead product from the batch kettle was temporarily stored in drums. The data in Table 4 show a gradual diminishing of volatile organics in this stream. Samples of overhead product were obtained at intervals of one hour.

Those drums from the batch kettle which contain mostly water are processed in the batch still. Materials charged to this still during the test were from a number of previous runs so no mass balance was attempted. The results are given in Table 5. The bottoms were about 95 percent water and required chemical treatment for the organics. The "solvent" in the receiver was about

Table 1. Analytical results for aqueous waste treatment.

Pollutant	Mixed Aqueous Influent #1	Mixed Aqueous Influent #2	Isolation Tank #1	Isolation Tank #2	Waste Acid	Gravity Thickened Sludge	Treated Effluent
METALS (mg/l)							
Cadmium	88	0.5	90	# <86	2.4	# 260	0.7
Hex. chromium	2.4	4.8	4,800	NS	NS	# NS	3.2
Total chromium	2,800	10.0	9,000	# 4,300	1,300	# 7200	1.6
Copper	300	9.0	780	# 74,000	96	# 940	5.0
Iron	660	3.0	1,900	# 12,000	6,700	# 2000	0.7
Lead	32	0.5	230	# 300	40	# 50	<0.5
Nickel	28	2.0	100	# 130	11	# 70	3.0
Zinc	40	0.2	130	# 18,500	56	# 80	0.2
EP TOXICITY (mg/l)							
Arsenic	NS	NS	NS	NS	NS	<0.10	NS
Barium	NS	NS	NS	NS	NS	<0.10	NS
Cadmium	NS	NS	NS	NS	NS	1.80	NS
Chromium	NS	NS	NS	NS	NS	0.09	NS
Lead	NS	NS	NS	NS	NS	<0.10	NS
Mercury	NS	NS	NS	NS	NS	<0.10	NS
Selenium	NS	NS	NS	NS	NS	<1.00	NS
Silver	NS	NS	NS	NS	NS	<0.20	NS
VOLATILE ORGANIC COMPOUNDS (μg/l)							
Methylene chloride	8,600	1,100	15,000	NS	NS	NS	750
Acetone	4,000	5,000	35,000	NS	NS	NS	12,000
2-Butanone (MEK)	100,000	210,100	4,000	NS	NS	NS	24,000
1,1,1-Trichloroethane	500	<100	200	NS	NS	NS	<100
Benzene	<100	<100	29	NS	NS	NS	<100
4-Methyl-2-pentanone	2,600	660	<100	NS	NS	NS	<500
Toluene	2,300	150	860	NS	NS	NS	160
Ethylbenzene	<100	<100	62	NS	NS	NS	<100
Total xylenes	<100	<100	200	NS	NS	NS	<100
ACID EXTRACTABLE COMPOUNDS (μg/l)							
2-Nitrophenol	<1,000	T <1,000	<20,000	NS	NS	NS	160
4-Nitrophenol	<1,000	<1,000	<20,000	NS	NS	NS	260
2,4-Dinitrophenol	<1,000	<1,000	<20,000	NS	NS	NS	30
Pentachlorophenol	T <1,000	<1,000	<20,000	NS	NS	NS	T <10
BASE/NEUTRAL EXTRACTABLE COMPOUNDS (μg/l)							
1,2-Dichlorobenzene	<1,000	<1,000	<20,000	NS	NS	NS	T <10
Naphthalene	T <1,000	<1,000	<20,000	NS	NS	NS	T <10
Bis(2-ethylhexyl) phthalate	T <1,000	T <1,000	<20,000	NS	NS	NS	<10
Di-n-butylphthalate	T <1,000	T <1,000	<20,000	NS	NS	NS	51

T = Trace concentrations detected below the average reporting limit.
NS = Not sampled.

units are mg/kg.

Table 2. Sludge TCLP results.

Pollutant	Raw Waste (Compositional)	TCLP
METALS (mg/l)		
Arsenic	NS	0.01
Barium	NS	0.20
Cadmium	# 252	5.50
Chromium	# 44,600	370.00
Lead	# 251	<0.10
Mercury	NS	<0.0002
Selenium	NS	<0.02
Silver	NS	<0.02
VOLATILE ORGANIC COMPOUNDS (μg/l)		
Chloromethane	<25	<50
Bromomethane	<25	<50
Vinyl chloride	<25	<50
Chloroethane	<25	<50
Methylene chloride	220	3.2
Acetone	3700	55
Carbon disulfide	<10	<20
1,1-Dichloroethene	<10	<20
1,1-Dichloroethane	<10	<20
Trans-1,2-dichloroethene	<10	<20
Chloroform	<10	<20
1,2-Dichloroethane	110	2.8
Methyl ethyl ketone	<50	<10
1,1,1-Trichloroethane	11	0.8
Carbon tetrachloride	<10	<20
Vinyl acetate	<10	<20
Bromodichloromethane	<10	<20
1,2-Dichloropropane	<10	<20
Trans-1,3-dichloropropene	<10	<20
Trichloroethene	<10	<20
Dibromochloromethane	<10	<20
1,1,2-Trichloroethane	<10	<20
Benzene	<10	<20
Cis-1,3-dichloropropene	<10	<20
2-Chloroethylvinylether	<10	<20
Bromoform	<10	<20
2-Hexanone	<50	<100
4-Methyl-2-pentanone	<50	<100
Tetrachloroethene	<10	<20
1,1,2,2-Tetrachloroethane	<10	<20
Toluene	19	11
Chlorobenzene	<10	<20
Ethylbenzene	<10	<20
Styrene	<10	<20
Total xylenes	<10	<20
Acrylonitrile	NS	ND
Isobutanol	NS	ND
Pyridine	NS	ND
1,1,1,2-Tetrachloroethane	NS	ND

# units are mg/kg.

Table 3. Main still analytical results.

Pollutant	MEK Solvent Clarified Solvent Influent	Settled Solvent Solids	Finished Water Product	Finished Solvent Product	Still Bottoms
PRINCIPAL ORGANIC COMPOUNDS (mg/l)					
Acetone	17,000	24,000	8,500	20,000	<2,500
n-Butanol	6,500	<2,500	<500	6,000	11,000
Dioxane	<2,500	<2,500	<500	<2,500	<2,500
Ethanol	<2,500	<2,500	8,400	<2,500	<2,500
Ethyl acetate	10,000	<2,500	<500	13,000	4,100
Isopropanol	27,000	16,000	9,000	41,000	9,600
Methanol	<2,500	<2,500	9,900	<2,500	<2,500
Methyl ethyl ketone (MEK)	850,000	190,000	4,400	910,000	500,000
Methyl isobutyl ketone (MIBK)	21,000	<2,500	<500	20,000	30,000
1,1,1-Trichloroethane	<2,500	<2,500	<500	<2,500	<2,500
Toluene	48,000	<2,500	<500	51,000	41,000
Total unidentified concentration	44,000	45,000	1,600	25,000	99,000
METALS (mg/l)					
Cadmium	8	# 240	NS	NS	# 620
Total chromium	22	# 820	NS	NS	# 2,200
Copper	4	# 38,000	NS	NS	# 270
Iron	16	# 3,400	NS	NS	# 1,200
Lead	16	# 870	NS	NS	# 2,200
Nickel	<0.3	# 1,900	NS	NS	# <130
Zinc	10	# 9,600	NS	NS	# 490
OTHER ANALYSES					
Chemical oxygen demand (mg/l)	NS	NS	NS	NS	I
Total organic halide (weight %)	0.400	0.000	0.002	0.470	0.500
Oil and grease (ppm)	180,000	NS	NS	NS	260,000
Total solids (ppm)	90,000	96,000	NS	NS	310,000
Total volatile solids (ppm)	82,000	38,000	NS	NS	290,000
Total suspended solids (ppm)	26,000	40,000	NS	NS	200,000
Total dissolved solids (ppm)	64,000	56,000	NS	NS	110,000
Total volatile suspended solids (ppm)	20,000	11,000	NS	NS	170,000
Total volatile dissolved solids (ppm)	62,000	27,000	NS	NS	120,000
Silica (weight %)	0.03	0.10	NS	NS	0.07
% Water (weight %)	6.43	62.70	59.94	12.82	3.48
Flashpoint (°F)	<75	NS	NS	NS	NS
Boiling range (°C)	75-95	NS	NS	NS	NS
% Carbon (weight %)	65	12	4	63	68
% Hydrogen (weight %)	11	10	7	11	10
Btu content (Btu/lb)	NS	545	NS	NS	14,188
Viscosity (cst)	NS	NS	NS	NS	4.3 @ 52C
Paint filter test	NS	Fail	NS	NS	Fail

# = Units are mg/kg.
I = Sample interference.
NS = Not sampled.

Table 4. Batch kettle distillation results.

Pollutant	Clarified Influent	Initial Overhead Product	Overhead Product 1:15 hrs	Overhead Product 2:30 hrs	Overhead Product 3:15 hrs
PRINCIPAL ORGANIC COMPOUNDS (mg/l)					
Acetone	84,000	92,000	20,000	4,100	3,200
n-Butanol	<2,500	<2,500	<2,500	<2,500	<2,500
Ethanol	<2,500	<2,500	<2,500	<2,500	<2,500
Isobutanol	<2,500	<2,500	<2,500	<2,500	<2,500
Isopropanol	67,000	110,000	35,000	12,000	10,000
Methanol	<2,500	<2,500	<2,500	<2,500	<2,500
Methyl ethyl ketone (MEK)	6,100	4,900	<2,500	<2,500	<2,500
Methyl isobutyl ketone (MIBK)	<2,500	<2,500	<2,500	<2,500	<2,500
1,1,1-Trichloroethane	<2,500	<2,500	<2,500	<2,500	<2,500
Trichloroethylene	<2,500	<2,500	<2,500	<2,500	<2,500
Toluene	<2,500	<2,500	<2,500	<2,500	<2,500
Total unidentified concentration	5,700	4,800	2,700	<2,500	<2,500
METALS (mg/l)					
Cadmium	<0.2	NS	NS	NS	NS
Total chromium	<0.3	NS	NS	NS	NS
Copper	1.8	NS	NS	NS	NS
Iron	0.4	NS	NS	NS	NS
Lead	<0.5	NS	NS	NS	NS
Nickel	<0.3	NS	NS	NS	NS
Zinc	1.4	NS	NS	NS	NS
OTHER ANALYSES					
Total organic halide (weight %)	0.033	0.140	0.003	0.027	0.020
Oil and grease (mg/l)	5,000	NS	NS	NS	NS
Total solids (mg/l)	5,100	NS	NS	NS	NS
Total volatile solids (mg/l)	4,400	NS	NS	NS	NS
Total suspended solids (mg/l)	70	NS	NS	NS	NS
Total dissolved solids (mg/l)	5,000	NS	NS	NS	NS
Total volatile suspended solids (mg/l)	66	NS	NS	NS	NS
Total volatile dissolved solids (mg/l)	4,300	NS	NS	NS	NS
Silica (weight %)	0.06	NS	NS	NS	NS
% Water (weight %)	83.60	83.36	89.44	95.75	95.99
Flashpoint (°F)	<75	NS	NS	NS	NS
Boiling range (°C)	74-106	NS	NS	NS	NS
% Carbon (weight %)	9	21	8	8	11
% Hydrogen (weight %)	11	12	11	12	11
Viscosity (cst)	1.1@3.5C	NS	NS	NS	NS

NS = Not sampled.

Table 5. Batch still reboiler results.

Pollutant	Still Bottoms	Finished Product	Thinning Tank Water
VOLATILE ORGANIC COMPOUNDS (mg/l)			
Methylene chloride	NS	NS	250
Acetone	NS	NS	180
2-Butanone (MEK)	NS	NS	31
1,1,1-Trichloroethane	NS	NS	20
4-Methyl-2-pentanone	NS	NS	3.6
Toluene	NS	NS	1.1
PRINCIPAL ORGANIC COMPOUNDS (mg/l)			
Acetone	2,600	7,200	NS
n-Butanol	1,700	4,500	NS
Dioxane	13,000	17,000	NS
Ethanol	10,000	29,000	NS
Isobutanol	<500	<2,500	NS
Isopropanol	7,400	47,000	NS
Methanol	5,800	<2,500	NS
Methyl ethyl ketone (MEK)	4,900	11,000	NS
Methyl isobutyl ketone (MIBK)	<500	<2,500	NS
1,1,1-Trichloroethane	2,000	<2,500	NS
Total unidentified concentration (ppm)	23,000	4,400	NS
ACID EXTRACTABLE COMPOUNDS (μg/l)			
2-Nitrophenol	NS	NS	24,000
BASE/NEUTRAL EXTRACTABLE COMPOUNDS (μg/l)			
Isophorone	NS	NS	5,800
METALS (mg/l)			
Cadmium	0.3	NS	<0.6
Total chromium	<0.3	NS	<0.9
Copper	27.0	NS	<1.8
Iron	1.0	NS	11.0
Lead	<0.5	NS	<1.5
Nickel	<0.3	NS	<0.9
Zinc	4.0	NS	<0.9
OTHER ANALYSES			
Chemical oxygen demand (mg/l)	I	NS	NS
Total organic carbon (mg/l)	NS	NS	12,000
Total organic halide (weight %)	0.030	0.065	0.000
Oil and grease (mg/l)	420	NS	1,600
Total solids (mg/l)	7,400	NS	40,000
Total volatile solids (mg/l)	1,400	NS	19,000
Total suspended solids (mg/l)	130	NS	1,300
Total dissolved solids (mg/l)	7,300	NS	39,000
Total volatile suspended solids (mg/l)	110	NS	820
Total volatile dissolved solids (mg/l)	1,300	NS	18,000
Silica (weight %)	0.13	NS	0.56
% Water (weight %)	95.33	88.65	NS
% Carbon (weight %)	2	6	NS
% Hydrogen (weight %)	11	11	NS
Btu content (Btu/lb)	<200	NS	NS
Viscosity (cst)	2.2@67C	NS	NS
Paint filter test	Fail	NS	NS

I = Sample interference.
NS = Not sampled.

89 percent water and could not be reused as solvent in this instance.

Cyanide Treatment

The influent waste treated in cells was a spent electroplating bath, characterized by the manifest as RCRA Waste Code F007. The initial cyanide concentration, shown in Table 6, was 16,100 mg/liter. The influent also contained copper at 7,100 mg/liter, zinc at 140 mg/liter, and lesser levels of iron, nickel, cadmium, lead, and chromium. Volatile organic compounds in the untreated waste were relatively low.

The cyanide concentrations in the electrolytic cells decreased only minimally during the 72-hour monitoring period (less than 15%). This batch actually required about 192 hours (8 days) processing time to reduce the concentration to 1000 mg/liter, according to plant personnel.

The alkaline chlorination data in Table 6 are from a previously treated electrolytic oxidation batch with an influent cyanide concentration of about 1400 mg/liter. The effluent cyanide concentration was 620 mg/liter. The poor efficiency may be attributable to copper and iron complexes which are difficult to treat. The formation of trihalomethanes during alkaline chlorination has been reported in several previous studies. The data from this study support these findings. Chloroform concentration increased from 10 to 6700 µg/liter, bromodichloromethane from less than 10 to 1700 µg/liter, and dibromochloromethane from less than 10 to 360 µg/liter. Methylene chloride, chloromethane, and trichloromethane also showed increases.

Cooling Tower

Results of the analyses on untreated ground waters, chilled effluent from the cooling tower, and an air sample taken in proximity to the tower are presented in Table 7. The overall percent removals of volatile organics partially reflect the recycling of the cooling waters. A well-developed slime layer was growing on the medium. Other studies have indicated that aerobic activity in cooling towers contributes to organic compound removal.

The air sample was collected in an evacuated cylinder and analyzed by gas chromatography/mass spectrometry (GC/MS). None of the organics in the air sample were present above their analytical detection limits in this sample.

Oily Wastewater Treatment

The chief objective of testing the centrifuge was to document its performance at thickening an oily wastewater treatment sludge. As shown in Table 8, the oil and grease content of the centrifuge feed was about 8 percent (83,000 ppm) and about 33 percent of the sludge cake. Of the 13 volatile organics quantified, xylenes were present in the highest concentration. The centrifuged cake contained about 20 percent water. The company uses this process to reduce the waste volume ultimately requiring land disposal.

The research described in this paper has been funded wholly or in part by the United States Environmental Protection Agency. It has been subjected to Agency peer and administrative review and approved for publication. However, the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Table 6. Cyanide treatment results.

Pollutant	Concentrated Cyanide Influent	Electrolytic Process Grab	Electrolytic Process Grab	Electrolytic Process Grab	Alkaline Chlorin. Influent*	Treated Alk-Cl Effluent*
TREATMENT DURATION (hours)	0	24	48	72	0	48
VOLATILE ORGANIC COMPOUNDS (μg/l)						
Chloromethane	<25	NS	NS	NS	<25	280
Methylene chloride	<25	NS	NS	NS	<25	550
Chloroform	<10	NS	NS	NS	10	6,700
1,2-Dichloroethane	46	NS	NS	NS	12	<100
2-Butanone	130	NS	NS	NS	52	<500
1,1,1-Trichloroethane	14	NS	NS	NS	<10	<100
Bromodichloromethane	<10	NS	NS	NS	<10	1,700
Trichloroethene	18	NS	NS	NS	89	740
Dibromochloromethane	<10	NS	NS	NS	<10	360
Toluene	21	NS	NS	NS	<10	<100
ACID EXTRACTABLE COMPOUNDS	ND	NS	NS	NS	NS	ND
BASE/NEUTRAL EXTRACTABLE COMPOUNDS						
Bis(2-ethylhexyl)-phthalate (μg/l)	<20	NS	NS	NS	<20	<2,000
METALS (mg/l)						
Cadmium	45.0	NS	NS	NS	55.0	NS
Total chromium	9.5	NS	NS	NS	15.0	NS
Copper	7,100.0	NS	NS	NS	1,000.0	NS
Iron	60.0	NS	NS	NS	25.0	NS
Lead	12.0	NS	NS	NS	<2.5	NS
Nickel	55.0	NS	NS	NS	10.0	NS
Zinc	140.0	NS	NS	NS	15.0	NS
OTHER ANALYSES						
Zinc (mg/l)	140.0	NS	NS	NS	15.0	NS
Total organic carbon (mg/l)	37,000	41,000	40,000	37,000	13,000	16,000
Total organic halide (weight %)	0.120	NS	NS	NS	0.090	0.350
Cyanide (mg/kg)	16,100	15,500	15,600	13,800	1,400	620
Free chlorine (mg/l)	NS	NS	NS	NS	NS	15
pH	12.5	12.5	12.5	12.5	12.0	NS
Temperature (°C)	5	NS	NS	NS	NS	NS

NS = Not sampled.
ND = Not detected.
* From different batch.

Table 7. Cooling Tower Results.

Pollutant	Units	Untreated Ground-water	Chilled Effluent	Percent removal	Air Sample Cooling Tower
VOLATILE ORGANIC COMPOUNDS (μg/l)					
Bromomethane		1,400	<12.5	>99	<250
Methylene chloride		190	<12.5	>93	<250
Acetone		2,000	<12.5	>99	<2,500
1,1-Dichloroethene		22	<5	>77	<100
1,1-Dichloroethane		270	<5	>98	<100
Trans-1,2-dichloroethene		6,300	160	98	<100
1,2-Dichloroethane		100	8	92	<100
2-Butanone		900	<25	>97	<500
1,1,1-Trichloroethane		1,700	200	88	<100
Trichloroethene		2,100	420	80	<100
Benzene		41	<5	>88	<100
4-Methyl-2-pentanone		1,200	<25	>98	<500
Tetrachloroethene		170	30	82	<100
Toluene		3,400	<5	>99	<100
Ethylbenzene		4,100	<5	>99	<100
Total xylenes		1,600	<5	>98	<100
Total unidentified		25,600	963	97	0
OTHER ANALYSES					
Total organic carbon (mg/l)		19	9	53	NS
pH		6	6	-	NS
Temperature (°C)		6	6	-	NS

NS = Not sampled.

Table 8. Results for sludge dewatering.

Pollutant	Centrifuge feed	Centrate	Sludge cake
VOLATILE ORGANIC COMPOUNDS (mg/kg)			
Methylene chloride	8,100	NS	NS
Acetone	26,000	NS	NS
1,1-Dichloroethene	<400	NS	NS
1,1-Dichloroethane	7,600	NS	NS
1,2-Dichloroethane	930	NS	NS
2-Butanone	9,900	NS	NS
1,1,1-Trichloroethane	40,000	NS	NS
Trichloroethene	8,100	NS	NS
Benzene	4,100	NS	NS
Tetrachloroethene	11,000	NS	NS
Toluene	59,000	NS	NS
Ethylbenzene	17,000	NS	NS
Total xylenes	96,000	NS	NS
ACID EXTRACTABLE COMPOUNDS (mg/kg)	ND	NS	NS
BASE/NEUTRAL EXTRACTABLE COMPOUNDS (mg/kg)			
Naphthalene	<125,000	NS	NS
Chrysene	<125,000	NS	NS
Phenanthrene	<125,000	NS	NS
OTHER ANALYSES			
Total solids (ppm)	275,100	226,200	605,500
Total volatile solids (ppm)	193,200	179,200	253,000
Total suspended solids (ppm)	202,600	144,100	564,100
Total dissolved solids (ppm)	72,500	82,100	41,400
Total volatile suspended solids (ppm)	137,600	108,100	217,800
Total volatile dissolved solids (ppm)	55,600	71,100	35,200
Oil and grease (ppm)	83,000	190,000	* 33
% Water (weight %)	NS	NS	20
% Carbon (weight %)	NS	NS	28
% Hydrogen (weight %)	NS	NS	7
Btu content (Btu/lb)	NS	NS	5,342
Paint filter test	NS	NS	Pass
Specific gravity @ 24°C (g/ml)	NS	0.97	1.14

* = Percent dry solids.
NS = Not sampled.
ND = Not detected.

APPENDIX

ANALYTICAL PROCEDURES AND REFERENCE SOURCES

ANALYTICAL PROCEDURES AND REFERENCE SOURCES

Measurement Parameter	Method No.	Title	Reference
Volatile Organics	Method 8240	GC/MS for Volatile Organics	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Semivolatile Organics	Method 8270	GC/MS Method for Semivolatile Organics: Capillary Coevnia Technique	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed, U.S. EPA, July 1982.
Organochlorine Pesticides and PCB's	Method 8080	Organochlorine Pesticides and PCB's	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Metals - Arsenic	Method 7060	Arsenic (Atomic Absorption, Furnace Technique)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Barium	Method 7080	Barium (Atomic Absorption, Direct Aspiration Method)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Cadmium	Method 7130	Cadmium (Atomic Absorption, Direct Aspiration Method)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Chromium	Method 7190	Chromium (Atomic Absorption, Direct Aspiration Method)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Lead	Method 7420	Lead (Atomic Absorption, Direct Aspiration Method)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Mercury	Method 7470	Mercury (Manual Cold-Vapor Technique)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Nickel	Method 7520	Nickel (Atomic Absorption, Direct Aspiration Method)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Silenium	Method 7740	Selenium (Atomic Absorption, Direct Aspiration Method)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Silver	Method 7760	Silver (Atomic Absorption, Direct Aspiration Method)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Cyanide - Total and Amenable	Method 9010	Total and Amenable Cyanide	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Total Organic Halide	Method 9020	Total Organic Halides (TOX)	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Sulfide	Method 9030	Sulfides	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
EP Toxicity	Method 1310	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test	Test Methods for Evaluating Solid Waste, SW-846, 2nd ed., U.S. EPA, July 1982.
Paint Filter Test	Method 9095	Update II to SW-846	Federal Register, Vol. 50, No. 83, Tuesday, April 30, 1985, p. 18370-18375.
Fluoride		Fluoride, Total (Colorimetric, SPADNS with Bellack Distillation)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.

(continued)

(continued)

Measurement Parameter	Method No.	Title	Reference
Residue - Total	Method 160.3	Residue, Total (Gravimetric, Dried at 103-105°C)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Filterable	Method 160.1	Residue, Filterable (Gravimetric, Dried at 180°C)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Non-Filterable	Method 160.2	Residue, Non-Filterable (Gravimetric, Dried at 103-105°C)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Volatile	Method 160.4	Residue, Volatile (Gravimetric, Ignition at 550°C)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Hexavalent Chromium	Method 218.5	Chromium, Hexavalent, Dissolved	Methods for Chemical Analysis of Water and
Chemical Oxygen Demand	Method 410.1	Chemical Oxygen Demand (Titrimetric, Mid-Level)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Organic Carbon - Total	Method 415.2	Organic Carbon, Total (low level) (UV Promoted, Persulfate Oxidation)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Oil and Grease	Method 310.1	Alkalinity (Titrimetric, Ph 4.5)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Silica	Method 370.1	Silica, Dissolved (Colorimetric)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
pH	Method 150.1	pH (Electrometric)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Temperature	Method 170.1	Temperature (Thermometric)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Alkalinity	Method 310.1	Alkalinity (Titrimetric, pH 4.5)	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.
Silica	ASTM C25	Chemical Analysis of Limestone, Quicklime, and Hydrated Lime	1984 Annual Book of ASTM Standards
Btu Content	ASTM D2015	Gross Caloritic Value of Solid Fuel by the Calibrated Bomb Colorimeter	1984 Annual Book of ASTM Standards
Water Content	ASTM D1364	Water in Volatile Solvents (Fischer Reagent Titration Method)	1984 Annual Book of ASTM Standards
Boiling Content	ASTM D 1078	Distillation Range of Volatile Organic Liquids	1984 Annual Book of ASTM Standards
Carbon, Hydrogen, Nitrogen	ASTM D 3178	Carbon and Hydrogen in the Analysis Sample of Coal and Coke	1984 Annual Book of ASTM Standards
Viscosity	ASTM D 4212	Viscosity by Dip-Type Viscosity Cups	1984 Annual Book of ASTM Standards
Principal Organic Components	GC, Direct Injection	See Assy Procedures for Specific Components	Reagent Chemicals: ACS Specifications, 6th ed.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

The Destruction of Hazardous Organic Waste Materials Using the MODAR Oxidation Process

Carl N. Staszak
Kenneth C. Malinowski, Ph.D
CECOS International, Inc.
Buffalo, New York 14207

William R. Killilea
Kathleen C. Swallow, Ph.D.
MODAR, Inc.
Natick, Massachusetts 01760

ABSTRACT

CECOS International, Inc., a hazardous waste treatment and disposal firm headquartered in Buffalo, New York, and MODAR, Inc. of Houston, Texas, conducted a field, pilot-scale demonstration in 1985 of the MODAR Oxidation Process for the destruction of hazardous organic waste materials.

The MODAR Oxidation Process utilizes water at conditions above its critical point (374°C and 218 atm.) as the reaction medium for the oxidation of organic materials. The products of this oxidation reaction, for a typical organic material, are carbon dioxide and water. Any halogen present as part of the organic matrix is converted to its halo-acid form.

Two waste streams were destroyed in the field tests. These were an aqueous-based waste contaminated with several organic EPA priority pollutants, and an organic transformer dielectric fluid contaminated with polychlorinated biphenyls (PCBs). In both tests, waste constituent concentrations in liquid and gas process effluents were below analytical detection limits. Destruction efficiencies based on influent concentrations and the reported detection limits were greater than 99.99%.

The results of the demonstration have shown the process' ability to destroy toxic and persistent organic contaminants in liquid waste streams without producing hazardous by-products.

INTRODUCTION

During the Summer of 1985, CECOS International, Inc. of Buffalo, New York, and MODAR, Inc. of Houston, Texas, conducted a field, pilot-scale demonstration of the MODAR Oxidation Process for the destruction of hazardous organic waste materials. The demonstration, performed at CECOS' Niagara Falls, New York Hazardous Waste Treatment and Disposal Facility, employed a skid-mounted oxidation unit, having a nominal organic material flow capacity of 50 gallons per day, for the destruction of two waste streams. These streams were an aqueous-based waste and an organic dielectric fluid containing polychlorinated biphenyls (PCBs).

The MODAR process for hazardous waste destruction uses water in its supercritical state (above 374°C and 218 atm) as the process medium for carrying out the destruction of organic materials by oxidation. Key to the success of the process is the fact that gases, including oxygen, and organic substances are completely soluble in supercritical water, whereas inorganic salts exhibit greatly reduced solubility under process conditions. Thus, it is possible to carry out oxidation reactions by dissolving organic substances and oxygen in the supercritical medium, thereby bringing them into intimate, single-phase contact at temperatures and molecular densities that allow conventional oxidation reactions to proceed rapidly to completion.

The process provides a method of rendering waste materials into non-hazardous compounds. Organic waste components are converted to carbon dioxide and water with potential recovery of the heat of oxidation, while inorganic components can be separated out as solid salts, and reused or safely discarded. Water, when present in the waste matrix, is recovered in a highly purified form. The wastes are treated in an enclosed system so that the escape of pollutants to the environment is only a remote possibility.

This paper describes the MODAR Oxidation Process, the objectives and performance of the test program, and the results of the demonstration.

PURPOSE

The MODAR process has several advantages over conventional processes for waste destruction. These include: the destruction of organic compounds, including chemically-stable materials (such as PCBs) is very high; the oxidation can be energy self-sufficient with as little as 2% organic concentration; and, excess energy may be easily recovered as steam. The process operates at conditions below which oxides of nitrogen are formed; the MODAR technology is self-scrubbing; and, inorganic contaminants such as salts and metals are separated from contaminated waste streams, thus substantially reducing waste volumes. It provides for beneficial recovery of valuable components of the waste material; i.e., water for reuse, energy as noted above and in some cases inorganic salts. The MODAR system is closed loop; any process upset shuts the system down and the effluents are contained, not released to the environment.

Bench and pilot-scale laboratory work performed by MODAR confirmed the effectiveness of the process on both pure chemicals and synthesized mixtures of chemicals. However, its applicability to "real world" hazardous waste materials was still undemonstrated at the pilot-scale. Through MODAR's affiliation with CECOS, a pilot-scale test on toxic waste material was envisioned, and ultimately realized.

APPROACH

Process Description

A schematic flow sheet for the MODAR process as applied to liquid wastes is presented in Figure 1.

The process consists of the following steps:

Feed

1. Organic waste materials in an aqueous medium are pumped from atmospheric pressure to the pressure in the reaction vessel.

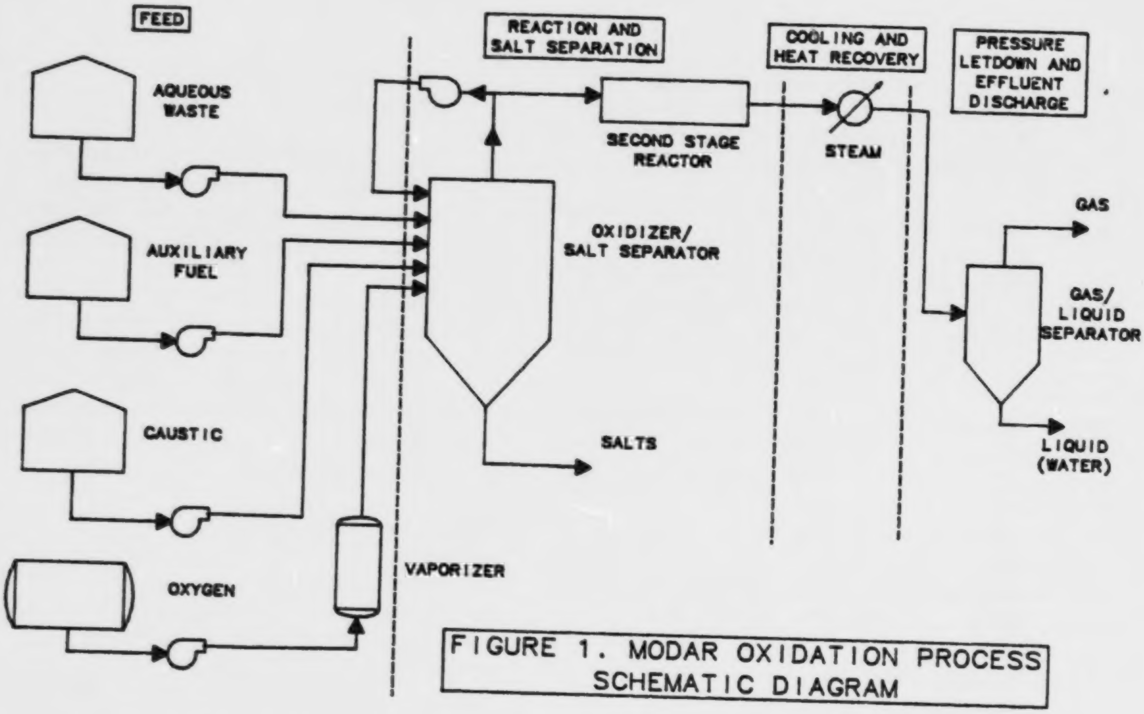

FEED
REACTION AND SALT SEPARATION
COOLING AND HEAT RECOVERY
PRESSURE LETDOWN AND EFFLUENT DISCHARGE
AQUEOUS WASTE
AUXILIARY FUEL
CAUSTIC
OXYGEN
VAPORIZER
SECOND STAGE REACTOR
OXIDIZER/ SALT SEPARATOR
SALTS
STEAM
GAS
GAS/ LIQUID SEPARATOR
LIQUID (WATER)

FIGURE 1. MODAR OXIDATION PROCESS SCHEMATIC DIAGRAM

2. Oxygen, stored as a liquid, is pumped to the pressure of the reaction vessel and then vaporized. Alternatively, air can be compressed to system pressure and metered into the reaction vessel.

3. Feed to the process is controlled to an upper limit of heating value of 1800 Btu/lb by adding dilution water or blending higher heating value waste material with lower heating value waste material prior to feeding to the reactor.

4. When the aqueous waste has a heating value below 1800 Btu/lb, fuel may be added in order to utilize a cold feed to the oxidizer.

5. Optionally, for wastes with heating value below 1800 Btu/lb, a combination of preheat by exchange with process effluent and fuel addition, or preheat alone may be used.

6. When organic wastes contain heteroatoms which produce mineral acids, and it is desired to neutralize these acids and form appropriate salts, caustic is injected as part of the feed stream.

7. A recycle stream of a portion of the supercritical process effluent is mixed with the feed streams to raise the combined fluid to a high enough temperature to ensure that the oxidation reaction goes rapidly to completion.

Reaction and Salt Separation

1. Because the water is supercritical, the oxidant is completely miscible with the solution (ie., the mixture is a single, homogeneous phase). Organics are oxidized in a controlled but rapid reaction. Since the oxidizer operates adiabatically, the heat released

by the readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized rapidly.

2. Since the salts have very low solubility in supercritical water, they separate from the other homogeneous fluids and fall to the bottom of the separation vessel where they are removed as a brine.

3. The gaseous products of reaction, along with the supercritical water, leave the reactor at its top. A portion of the supercritical fluid is recycled to the oxidizer by a high temperature, high pressure pump. This operation provides for sufficient heating of the feed to bring the oxidizer influent to optimum reactor conditions.

4. The remaining reactor effluent (other than that recycled), consisting of supercritical water and carbon dioxide, is cooled to discharge carbon dioxide and water at atmospheric conditions.

Cooling and Heat Recovery

1. Most of the heat contained in the effluent can be used to generate steam for use outside of the MODAR Process.

2. The heat remaining in the effluent stream can be used for lower level heating requirements or else be dissipated.

Pressure Letdown

1. The cooled effluent from the process separates into a liquid water phase and a gaseous phase. The latter contains primarily carbon dioxide along with that amount of oxygen in excess of the stoichiometric requirements (and nitrogen when air is the oxidant).

2. The separation is carried out in multiple stages in order to minimize erosion of valves as well as to optimize equilibria.

3. Salts are removed from the separator as a cool brine through multiple letdown stages and are either dried (and water recovered) or discharged, depending upon operating requirements.

Sampling and Analysis

During a demonstration run key performance parameters are continuously monitored using on-line analytical instruments or periodic grab samples. These parameters include:

1. Effluent gas carbon monoxide concentration measured with an on-line non-dispersive infrared analyzer. Low carbon monoxide concentrations indicate high waste oxidation efficiency.

2. Liquid effluent total organic carbon (TOC) measured with an on-line TOC analyzer.

3. Liquid effluent chloride concentration measured on grab samples with a chloride ion selective electrode. Chloride is produced from the oxidation of chlorinated organic compounds such as chlorophenol. The ionic chloride remains dissolved in the process' liquid effluent and is an indication of destruction of the chlorinated organics.

In addition to the continuous monitoring an expanded sampling and analysis program was designed to provide data for the calculation of waste destruction efficiencies. For this demonstration the expanded program included:

1. Analysis of each waste stream before the run for pH, TOC, total organic chlorine and the purgeable, acid and base/neutral fractions of the priority pollutant compounds. The PCB waste was also analyzed for PCBs. The data from these analyses and the feed flow rates were used to calculate the mass feed rate for each component, from which the destruction efficiency was calculated.

2. Analysis of a sample of the liquid effluent, which had been composited throughout each waste test, for pH, TOC, inorganic chloride and the purgeable, acid and base/neutral fractions of the priority pollutant compounds. The liquid effluent from the PCB test was also analyzed for PCBs. The data from these analyses and the liquid effluent flow rates were used to calculate the liquid mass effluent rate for each component.

3. Analysis of the extracts from XAD-2 resin traps, which were placed in the gaseous effluent lines during each waste test. The extract from each trap was analyzed for acid and base/neutral compounds. The data from these analyses, the volume of gas passed through each trap and the gaseous effluent flow rates, was used to calculate the gaseous mass effluent rate for each compound.

Waste destruction efficiencies were calculated for the individual hazardous compounds. The waste destruction efficiency is defined as:

$$e_d = \frac{M_{fi} - (M_{gi} + M_{li})}{M_{fi}} \times 100\% \qquad (1)$$

where:

e_d = destruction efficiency, %

M_{fi} = mass feed rate of component i to the unit, g/min

M_{gi} = mass effluent rate of component i in the gaseous effluent from the unit, g/min

M_{li} = mass effluent rate of component i in the liquid effluent from the unit, g/min

System Design

The pilot-scale unit's major components, as shown in the schematic of Figure 2, are grouped into modules. The first component is the system air compressor, followed by the stainless steel water reservoir and pump. Next, the aqueous and organic waste modules, consisting of stainless steel holding tanks and pumps, are each surrounded by splash barriers. These components also are separated from the hot zone by a floor-to-ceiling steel bulkhead. Within the hot zone itself, the start-up heaters, reactor, and heat exchangers are contained in Marinite-insulation enclosures. Upon leaving the hot zone, the process stream enters the pressure letdown module containing the liquid- vapor separators and the stainless steel effluent reservoir.

Another steel bulkhead separates the letdown modules from the two Hoffmann boxes containing the module's electrical connections. Each Hoffmann box is individually purged with air. The system is designed to process 50 gallons of organic, or 250 gallons of 10% organic in an aqueous medium, per day with a total throughput:waste ratio of up to 30:1.

Permitting

A permit for the temporary

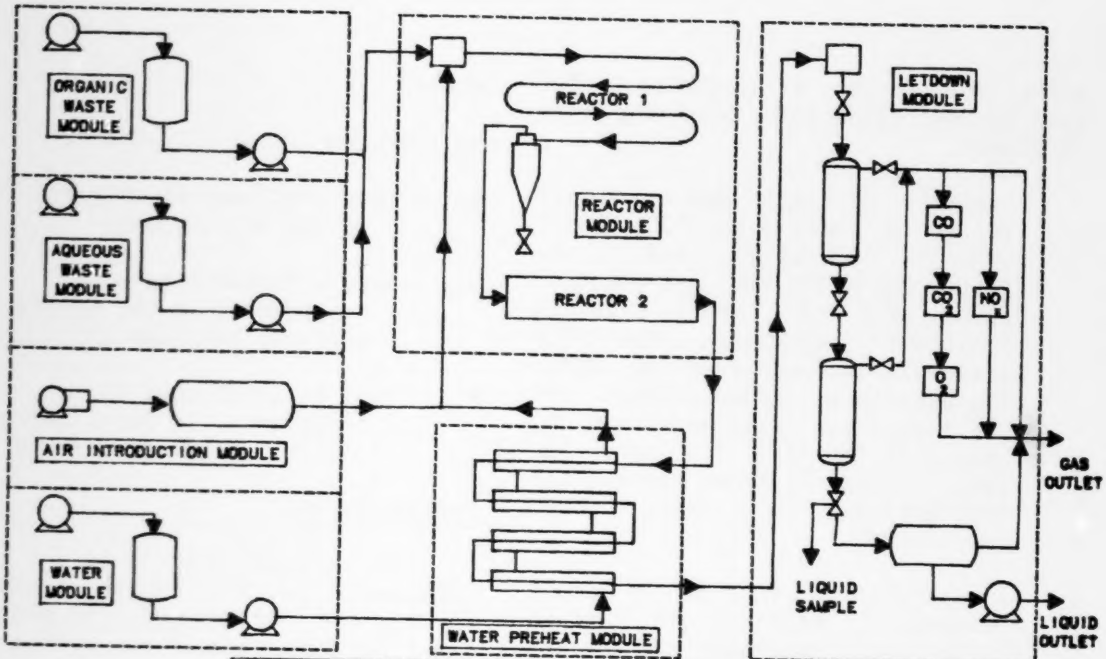

ORGANIC WASTE MODULE
REACTOR 1
REACTOR MODULE
AQUEOUS WASTE MODULE
REACTOR 2
AIR INTRODUCTION MODULE
WATER MODULE
WATER PREHEAT MODULE
LETDOWN MODULE
CO
CO_2
NO_x
O_2
GAS OUTLET
LIQUID SAMPLE
LIQUID OUTLET

FIGURE 2. PILOT-SCALE UNIT ARRANGEMENT

operation of the MODAR Oxidation Process at CECOS' Niagara Falls, New York Facility was required by the New York State Department of Environmental Conservation (NYSDEC), and was received from the Department in September, 1984. Formal authorization was requested from the United States Environmental Protection Agency (USEPA) for the use of a PCB-contaminated material for research and development purposes. This authorization was received in October, 1984.

Figure 3 shows a plot plan of the installation with the major operating areas identified. The MODAR Oxidation Process demonstration unit is skid-mounted and designed to be transportable by truck. The unit measures 40'0" x 8'6" x 9'8". It has been designed and constructed to meet Class I, Division 2 electrical codes.

Inspection and Testing

Following installation of the unit, NYSDEC inspections were performed to ensure permit compliance. The NYSDEC verified that all appropriate safety, health and environmental procedures were in place. They also witnessed a hydrostatic pressure test of all zones of the system.

MODAR subsequently conducted a short term operational test to verify organic destruction by oxidizing isopropyl alcohol (IPA). On-line instrumentation for temperature, pressure, flow and level measurements, and gas and liquid analyses were also checked.

Aqueous Waste Destruction Test

The waste destroyed by the process was a dilute isopropyl alcohol stream contaminated with trace quantities of several other pollutants. In order to increase the organic content of the waste, as well as to provide compounds that could be traced for calculation of destruction efficiencies, three organic compounds were added to the organic matrix: 1,1,2-trichloroethane, nitrobenzene,

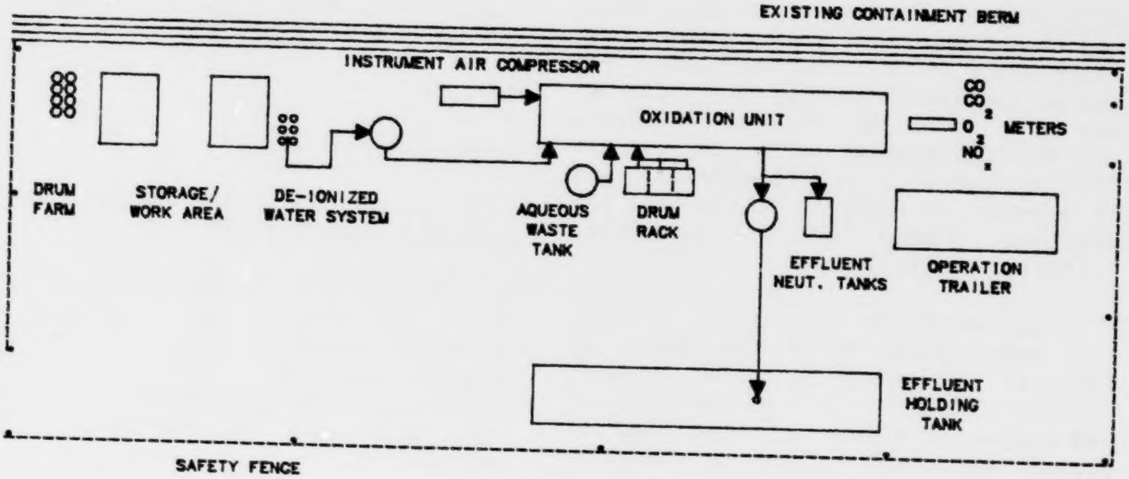

EXISTING CONTAINMENT BERM
INSTRUMENT AIR COMPRESSOR
OXIDATION UNIT
CO
CO2
O2
NOx
METERS
DRUM FARM
STORAGE/ WORK AREA
DE-IONIZED WATER SYSTEM
AQUEOUS WASTE TANK
DRUM RACK
EFFLUENT NEUT. TANKS
OPERATION TRAILER
EFFLUENT HOLDING TANK
SAFETY FENCE

FIGURE 3. MODAR OXIDATION PROCESS DEMONSTRATION PLOT PLAN

and 2-chlorophenol. Table 1 shows the concentrations of the major constituents (except for the alcohol) in the synthesized waste.

Since the waste had a TOC content of only 1%, it was clear that it was not concentrated enough for the exothermic oxidation reaction to maintain the temperatures necessary for complete oxidation of the organic compounds. For this reason, IPA was fed to the reactor along with the wastewater as a supplemental fuel source. At steady state, the waste oxidation temperature was in the range of 615 to 635°C. Approximately 145 operating hours were logged during this phase of the demonstration, and approximately 900 gallons of waste were processed through the unit.

Table 1 Synthesized Aqueous Waste Composition

Compound	Concentration (ug/L)
2-chlorophenol	1,200,000
Nitrobenzene	1,100,000
1,1,2-trichloroethane	190,000
Chloroform	1,000
Carbon Tetrachloride	590
Total Organic Carbon	10,300,000

Organic Waste Destruction Test

The organic waste destroyed by the unit was a transformer dielectric fluid containing polychlorinated biphenyls. The concentration of the PCBs in the fluid was 1600 mg/L on an Aroclor 1260 basis. This value was used as the basis for all destruction efficiency calculations.

As in the dilute aqueous waste test, the MODAR demonstration unit was started by heating process air and water. When oxidation of a clean mineral oil, mixed with an appropriate amount of dilution water, raised the operating temperatures to optimal levels, the PCB contaminated oil flow was started. At steady state, oxidation temperatures were in the range of 600 to 624°C.

Due to the high endothermic heat

of mixing between supercritical water and the compressed air oxidant, the temperature at the reactor inlet was cooler than optimum. For this reason, the rate at which the cold organic waste/dilution water was fed to the unit was cut back to approximately 50% of capacity in order to ensure that the reaction stayed within prescribed oxidation temperatures.

Approximately 95 hours of running time were logged during this phase of the test, bringing the total elapsed running time for the demonstration to 240 hours. A volume of 87 gallons of organic waste was oxidized by the unit.

PROBLEMS ENCOUNTERED

During the performance of the demonstration, mechanical and electrical failures were experienced on the MODAR Oxidation Unit. However, the upsets were of a minor nature, and were all detected and accounted for by the system's process control system. At no time was there an opportunity for contaminated materials to escape to the surroundings.

RESULTS

Aqueous Waste Test

The results of the aqueous waste test are summarized in Table 2.

Because all of the compounds were either analytically not detected or below the detection limit in both the liquid and gas effluents, the laboratory's standard detection limits have been used as the basis for calculation.

The calculated destruction efficiencies ranged from 99.997% to 99.998% for the major constituents. This should not be construed as the best obtainable destruction efficiency for the process, but is the maximum possible value computed using the fixed influent concentrations and effluent analytical detection limits. In fact, no organic compounds were

Table 2
Waste Destruction Efficiencies
MODAR/CECOS Demonstration

Contaminant	Feed Rate (g/min x 10^3)	Liquid Effluent Rate (g/min x 10^6)	Gaseous Effluent Rate (g/min x 10^6)	Destruction Efficiency %
Aqueous Waste Test				
2-chlorophenol	490	<9.7	<4.9	>99.997
Nitrobenzene	440	<5.6	<2.8	>99.998
1,1,2-TCE	77	<15	(A)	>99.981 (B)
Chloroform	0.40	<4.7	(A)	>98.83 (B)
Carbon Tetrachloride	0.24	<8.3	(A)	>96.53 (B)
Organic Waste Test				
PCB	91	<0.31	<4.4	>99.9949

Notes:
(A) Not analytically recoverable from gas sorbent tubes.
(B) Destruction efficiency based only on liquid analysis.

found above the analytical detection limit in the gas or liquid effluents. Meaningful destruction efficiencies of the minor components cannot be determined because of their low waste feed concentration values. At the conclusion of the aqueous waste test, the liquid effluent composite was shown to contain less than 1 mg TOC/L. Effluent gas carbon monoxide concentrations were always less than 10 ppm.

Elemental mass balances were calculated for carbon, oxygen and chlorine. Table 3 lists mass rates and closure of balances.

Organic Waste Test

Table 2 also summarizes the PCB destruction efficiency based on the test effluent analyses. PCBs were not detected in either gas or liquid effluent. A destruction efficiency of 99.995% was calculated, a value which does not represent the maximum obtainable efficiency, but rather a maximum that can be calculated for this instance given the feed concentration and analytical detection limits. Overall elemental mass balances for carbon, oxygen and chlorine are shown in Table 4.

CONCLUSIONS

The performance of, and the results from, the MODAR Oxidation Process Demonstration program have shown that:

1. The scale-up of the process from bench-to-pilot-scale was performed effectively and with no loss in process efficiency;

2. The process can be operated as a closed loop system, thereby preventing inadvertent releases of potentially toxic materials to the environment;

3. The pilot-scale unit can be operated on a long-term basis while maintaining suitable effluent quality;

4. The process can oxidize organic contaminants in an aqueous matrix to non-detectable levels;

5. Similarly, the process can oxidize organic contaminants in an organic liquid matrix, notably PCBs.

It is expected that future cooperation between CECOS and MODAR will result in the possibility of a second demonstration, with the long-term goal being a full-scale installation at one of CECOS' processing facilities.

ACKNOWLEDGEMENTS

CECOS and MODAR would like to thank both the USEPA Region II and NYSDEC Region IX staffs for their cooperation in the performance of this demonstration.

Table 3
Elemental Mass Balance Summary
Dilute Aqueous Waste

Element	Mass in (g/min)	Mass Out (g/min)	Closure %
C	44.4	42.8	96
O	296	298	101
Cl	0.196	0.200	102

Table 4
Elemental Mass Balance Summary
Organic Waste

Element	Mass in (g/min)	Mass Out (g/min)	Closure %
C	49	48	98
O	251	278	111
Cl	0.055	0.071	129

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REMEDIAL ACTION OF HYDROCARBON CONTAMINATION IN THE GLACIAL DRIFT DEPOSIT

BY

JAN WILK AND WLADYSLAW SKALNY

DEVELOPMENT CENTER FOR CHEMICAL RAW MATERIALS IN CRACOV, POLAND

ABSTRACT

This case study depicts an underground oil-recovery treatment system designed and installed in a petrochemical plant area to contain a hydrocarbon product in complex subsurface conditions. A loss of petroleum product from storage tanks and pipelines to the groundwater flow system in the glacial drift deposits has caused significant groundwater degradation in this area. The behavior and ultimate fate of hydrocarbons and their dissolved pollutant plumes become dependent on hydrogeological factors such as geology, groundwater bearing zones, and their interconnection. Test borings were drilled and soil and groundwater samples were collected to develop a comprehensive oil-recovery system The test borings were used to determine the magnitude of contaminated soils and preliminary locations of the monitoring wells. Selected test borings were converted into monitoring wells. Monitoring wells defined the areal extent of the free-floating hydrocarbon product and migration of the dissolved hydrocarbon in the groundwater flow system. Based on these data, an underground oil recovery system was designed and implemented. The system successfully recovered most of the free-floating hydrocarbon and abated the subsurface contamination.

INTRODUCTION

A large petrochemical plant, the subject of this paper, is experiencing problems with groundwater and soil contamination by hydrocarbon products and associated fire hazards. Such problems are typical for plants of this type. Remedial investigations were conducted to define contamination problems and design hydrocarbon recovery and treatment systems.

Remedial action has been taken to prevent fires and possible explosions as well as to protect groundwater and institute preventive measures. It is noted that, in comparison with two other plants of this type and size, located in the neighboring countries of Czechoslovakia and East Germany, the contamination of groundwater at this plant site is considerably reduced. If in those countries the quantity of free hydrocarbon products on the groundwater table was calculated as in excess of 100,000 m^3(2, 3), it was ten times less in this case.

This difference can be attributed to differences in the location of the local sewage systems as well as to differences in general hydrogeological conditions.

For this petrochemical plant, a secondary, very significant problem was prevention of the large groundwater well supply from receiving contaminated water by soluble hydrocarbon compounds. The existing municipal well is located a few kilometers from the plant area (Fig. 1) and supplies a medium-size city with a good quality of water. It was important to prevent this well from becoming contaminated with soluble hydrocarbon components because the municipal well was located in the only area in which sufficient yield and good water quality could be found. Fortunately, there was no contamination at that time, as shown by the results of widespread water-quality investigations. The typical characteristics of the subsurface pollution at the plant site and in the vicinity are hydrocarbon products (gasoline, fuel oil, and xylene) floating upon the water table and soluble compounds (mainly aromatic hydrocarbons).

PURPOSE

Several hydrogeological maps were prepared for the study area to determine subsurface contamination and its extent before the remedial action was implemented. These maps are based on hydrogeological data obtained from more than 300 test borings and 150 monitoring wells. Monitoring wells encountered thick hydrocarbon layers floating on the water table in the vicinity of the plant's underground utilities in fenced plant areas. Soluble hydrocarbon components were found under four-fiths of the plant area. Because of fire hazards and the possibility of damage of underground utility systems (electrical conduits, pipe fittings) in the floating hydrocarbon areas (pools), remedial action was undertaken to recover hydrocarbon product in these areas.

TECHNICAL APPROACH

Remedial action was preceded by detailed studies of the site hydrogeology, including aquifer transmissivities, confining layer occurrence, recharge and discharge areas for the aquifers, groundwater contamination, and hydrocarbon physical parameters such viscosity, density and sometimes temperatures. It should be noted that the temperature records in monitoring were very useful parameters for the assessment of the hydrocarbon recovery system. Taking into account all the results of the study and considering the fact that the surface of free hydrocarbon layers was only 4 to 7m beneath the ground surface, the use of recovery well systems was accepted as the best method of remedial action. Experimental pumping of pure hydrocarbon product was performed in two large hydrocarbon "pools," which appeared in different hydrogeological conditions. Operations proceeded first with pumping hydrocarbon product only and then progressed to pumping both hydrocarbon product and groundwater. Hydrocarbon product and groundwater was pumped out using two different recovery systems. The first system used one recovery well to pump both water and hydrocarbon. The system consisted of a pair of wells. The first well was used to pump only groundwater and the second, only hydrocarbon.

PROBLEMS ENCOUNTERED

A problem arose in handling xylene during experimental pumping. The xylene caused deterioration of the cables, hoses, and fittings of the pumps. This problem was partially solved by frequently changing parts in the pumps and by servicing them every 10 days. A second problem that arose involved the need to pump hydrocarbon product in the plant area close to the underground working facilities. Because of the low permeability of soils in this area, oil product could not be withdrawn. This is contrary to problems in Czechoslovakia and East Germany where hydrocarbon product occured in the high permeable aquifer, this product can be pumped outside of the plant area.

RESULTS

Remedial actions were conducted in two areas of hydrocarbon "pools"--Nos. 1 and 2. The remedial action started in area No. 1. Initial data from two wells installed in this area showed the thickness of the hydrocarbon layer to be 2 to 3m (diesel oil and fuel oil), which suggested that a large hydrocarbon pool occurred in area No. 1. On closer examination, however, it was proved that the till deposit, ranging from 2 to 5m thick, was underlain by the large lens of fine-grained sand (about 2.5 acres in area) with very low permeability. The hydrocarbon product was accumulated in the upper portion of the sand lens. The experimental pumping, using both methods mentioned in this paper, failed as a result of both the high viscosity of oil (3 to 6 times more than water) and the low specific yield of till with sand (0.5 to 0.1 liter/day). The recovery of oil product from hydrocarbon "pool" No. 1 was continued by using hand pumps to periodically remove accumulated oil from monitoring wells and recovery wells. Similar methods of oil withdrawal were used for those small hydrocarbon "pools" with high viscosity of oil product. These pools were not thick enough to create a cone of depression by pumping groundwater.

Hydrocarbon pool area No. 2 was observed for the last 2 years before remedial action was implemented. The area of hydrocarbon spill was 0.1 km^2 and the total amount of hydrocarbon was estimated to be more than 2,000 m^3 although detailed calculations have not been made (1). The average thickness of the hydrocarbon layer was determined through the hydrocarbon measurement in 25 wells. The variability of hydrocarbon thickness in monitoring wells during the pumping period is shown in Figure 2. The oil products (gasoline in the northern and central part of hydrocarbon "pool" and xylene in the discharge area) have low viscosity (0.7 compared to water). This hydrocarbon "pool" was one of the biggest sources of groundwater contamination by soluble aromatic hydrocarbons. In selecting the best method of recovery, two pumping stands were prepared (Figs. 3, 4, and 5) wherein a series of pumping tests were performed. The results of these tests are shown in Tables 1 and 2. Conclusions drawn from the pumping test results indicated that the effects of hydrocarbon recovery were influenced by three factors:

1. Hydrogeological conditions (vertical change in permeabilities and magnitude of hydraulic conductivity in the upper sand unit of hydrocarbon zone).
2. Well construction and well systems (one well with two pumps or two wells with one pump each).
3. Hydrocarbon product and groundwater pumping regime.

A nonproportional dependence was observed between the quantity of pumped oil and water (Fig. 6). Experience gained during testing was used to improve the construction wells. Water "intrusions" occurred during pumping of hydrocarbon product. Therefore specially designed well screens with pneumatic packers were used.

It was determined that the most efficient hydrocarbon recovery system consisted of two single-recovery wells. It was also determined that the distance between these two wells should be less than 0.5m and that the well screen interval and construction should eliminate undesired "water intrusion" during well pumping. The removal of a hydrocarbon "pool," according to applied technology in this case, was successfully accomplished, and the recovery process will last for a long time because of the large size of hydrocarbon "pools."

As a general conclusion, it is suggested that the possibility of groundwater contamination be studied before facilities are constructed or expanded. It may be possible to take better advantage of the results of geotechnical test borings and to undertake measures to protect against the possibility of subsurface contamination.

ACKNOWLEDGMENTS

This paper is published with the permission of the President of the Development Center for Chemical Raw Materials.

REFERENCES

1. Concave, 1979. Protection of groundwater from oil pollution. Concave Report 3/79: Den Haag, Holland April.
2. Schmidt, H., and O. Heiman, 1977. Grundwasserverunreinigungen durch Mineralol-Ursachen und technische Moglichkeiten zur Bekampfung. Wasserwirtschaftstechnik 2/77, Germany.
3. Pelikan, V., 1978 "Hydraulic protection of groundwaters against oil substances." Proceedings of International Symposium on Groundwater Pollution by Oil Hydrocarbons, Prague, Czechoslovakia, June.

DISCLAIMER

The work described in this paper was not funded by the U. S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

FIG. 1

SITE LOCATION AND GENERALIZED HYDROGEOLOGICAL CROSS-SECTION

1-glacial till, 2-static water level of first water-bearing zone, 3-static water of water level of second water-bearing zone, 4-probable directions of contamination

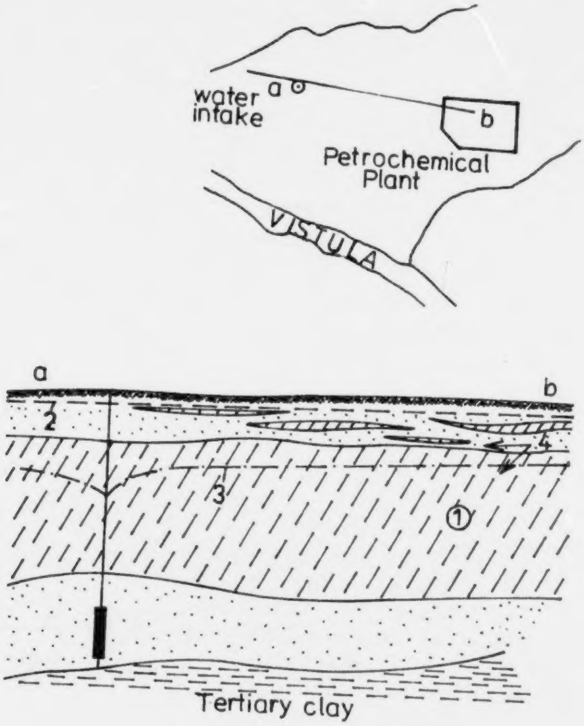

water intake
a
b
Petrochemical Plant
VISTULA
a
b
2
4
3
①
Tertiary clay

FIG. 2

VARIABILITY OF HYDROCARBON THICKNESS IN MONITORING WELLS DURING PUMPING PERIOD

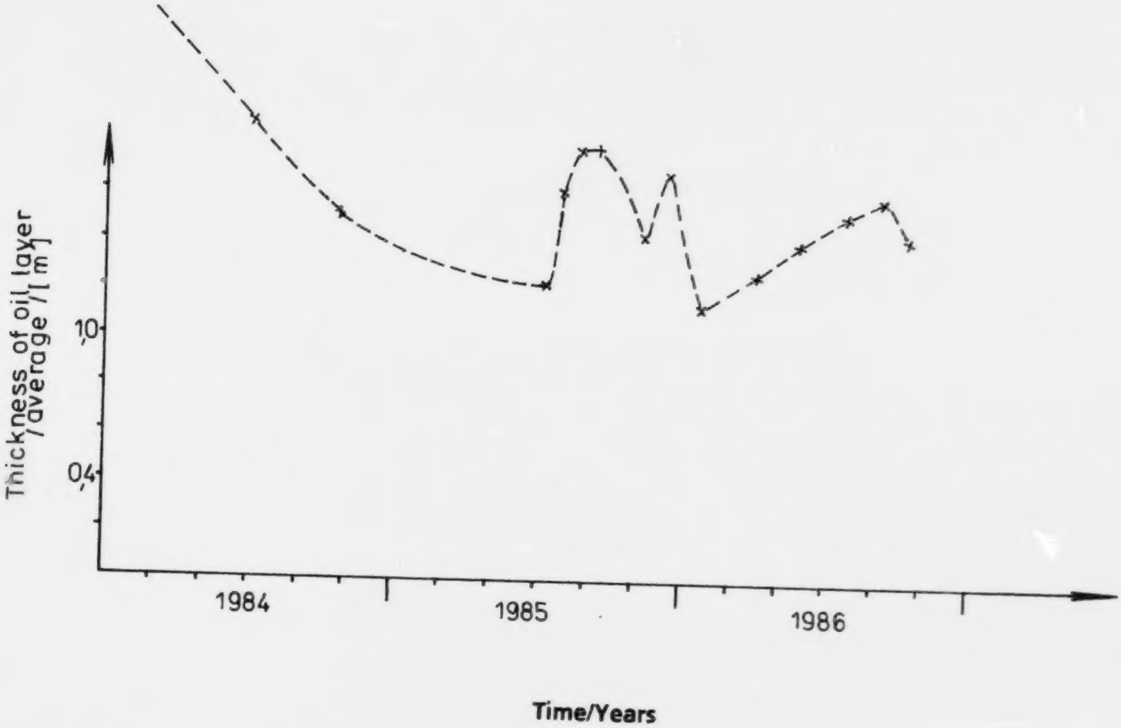
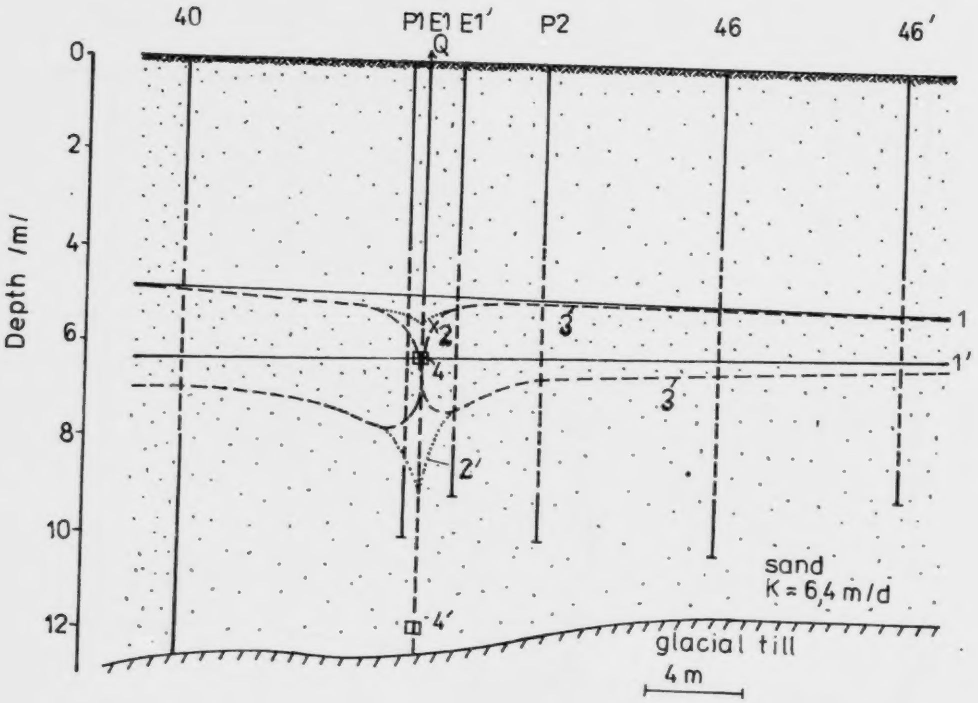


FIG. 3

CONFIGURATION OF HYDROCARBON PRODUCT AND GROUNDWATER LEVELS IN PUMPING STAND I (ONE RECOVERY WELL UTILIZING TWO-PUMP SYSTEM)

OIL RECOVERY - 0.05 m^3/HR (50L/HR)

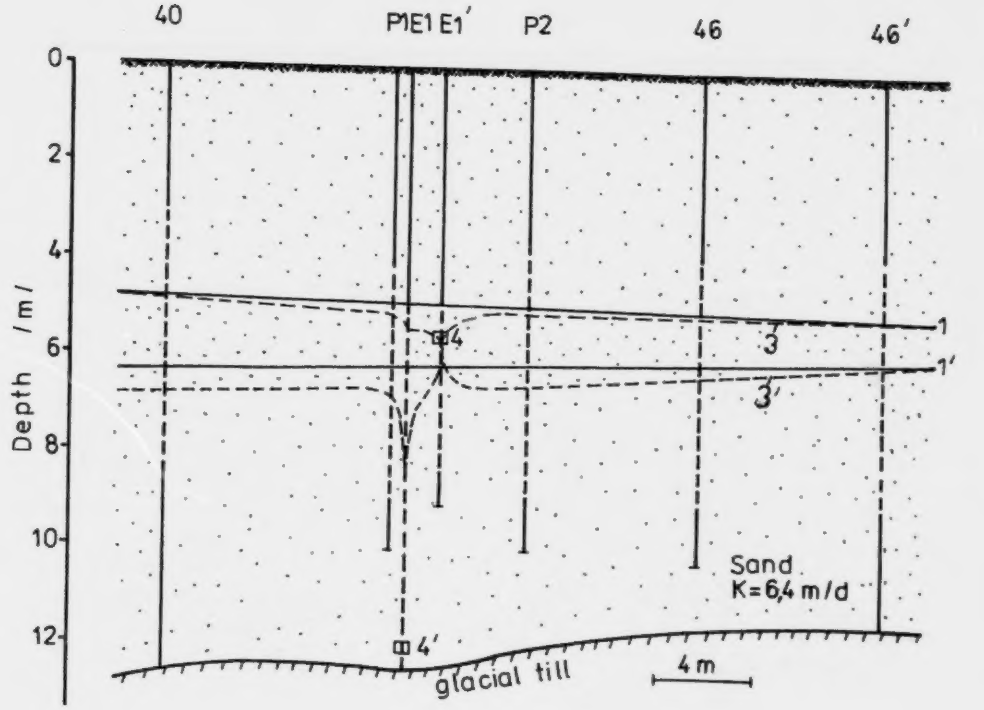
WATER RECOVERY - 8.5 m^3/hr


40
P1 E1 E1'
Q
P2
46
46'
Depth /m/
0
2
4
6
8
10
12
1
1'
2
2'
3
3
4
4'
sand
K = 6,4 m/d
glacial till
4 m

E1, E1'	**Recovery wells**
P2, P40	**Monitoring wells**
1, 1'	**Static hydrocarbon product and water-table level**
2, 2'	**Static hydrocarbon product and water-table level during pumping of hydrocarbon product level**
3, 3'	**Static hydrocarbon product and water-table level during pumping of oil and water**
4, 4'	**Pump's position**

FIG. 4

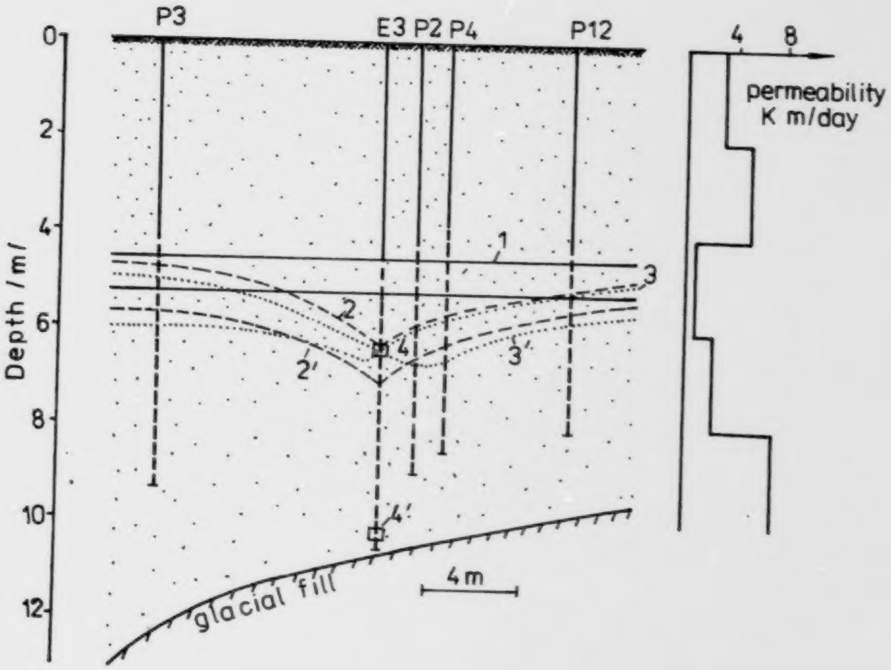
**CONFIGURATION OF HYDROCARBON PRODUCT
AND GROUNDWATER LEVELS IN PUMPING STAND I
(TWO RECOVERY WELLS UTILIZING ONE-PUMP SYSTEM)
OIL RECOVERY - 0.065 m³/HR (65L/HR)
WATER RECOVERY - 4.3 m³/HR**


40
P1E1 E1'
P2
46
46'
0
2
4
6
8
10
12
Depth /m/
1
1'
3
3'
4
4'
Sand
K=6,4 m/d
glacial till
4 m

E1, E1'	**Recovery well**
P2, P4	**Monitoring wells**
1, 1'	**Static hydrocarbon product and water-table levels**
2, 2'	**As above during pumping of water only**
3, 3'	**As above during pumping of hydrocarbon product only**
4, 4'	**Pump's position**

FIG. 5

CONFIGURATION OF HYDROCARBON PRODUCT AND GROUNDWATER LEVELS IN PUMPING STAND II (ONE RECOVERY WELL UTILIZING TWO-PUMP SYSTEM)
OIL RECOVERY - 0.020 m^3/HR (20L/hr)
WATER RECOVERY - 9 m^3/hr


P3
E3 P2 P4
P12
0
2
4
6
8
10
12
Depth / m /
1
2
2'
3
3'
4
4'
glacial fill
4m
4
8
permeability
K m/day

ES	**Recovery well**
P3, P4	**Monitoring wells**
1^F, 1^1	**Static hydrocarbon product and water-table levels**
2, 2^1	**Static hydrocarbon product and water-table levels during pumping of water only**
3, 3^1	**Static hydrocarbon product and water-table levels during pumping of hydrocarbon product only**
4, 4^1	**Pump's position**

FIG. 6

CORRELATION BETWEEN CAPACITY OF PUMPED OIL AND WATER (STAND I)

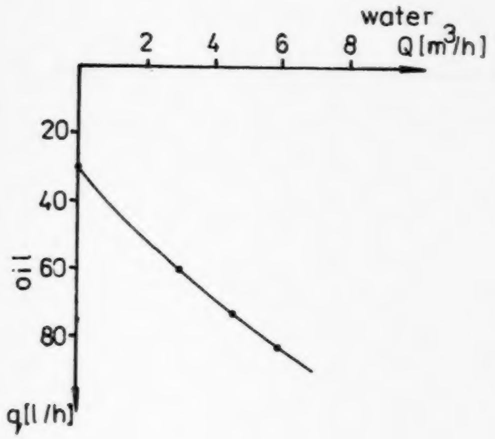


TABLE 1

COMPARISON OF PUMPING STANDS

Stand	Hydrogeological Conditions				Pumping Data		
	Well Locations in Hydrocarbon Pool Area	Average Aquifers Permeability (m/day)	Permeability Relation: Oil Layer to Bottom of Horizon	Thickness of Hydrocarbon Layer (m)	Pumping Rate of Water (m^3/hour)	Pumping Rate of Hydrocarbon Product (liter/hour)	Relation of Pumped Water to Hydrocarbon Product (m^3/m^3)
I	Central part	6,4	1:2	1,3	5,3	70	72
II	Area of drainage	3,3	1:7	0,8	9,2	20	620

TABLE 2

COMPARISON OF RESULTS OF PUMPING WITH THE METHODS OF PUMPING

Stand	Methods of Pumping			Results of Pumping			
	One Recovery Well Pumping Hydrocarbon Only	One Recovery Well Using Two Pumps	Two Pumps Using Two Recovery Wells in Distance Between Wells (m)	Pumping Rate of Water (m^3/hour)	Pumping Rate of Hydrocarbon (liter/hour)	Quantity of Pumped Water to Hydrocarbon (m^3/m^3)	Increment Quantity of Pumped Hydrocarbons (%)
I	x				30 (1)		
		x		8.6	57	134.6	90
			4	5.4	50	87.2	67
			1.3	4.5	75	53.5	250
			1.3 (3)	4.6	86	61.4	286
II	x				5 (2)		
		x		6.2	30	289	
			1.0	12.6	46	561	
			2.5	5.5	12	685	

(1) There was an observed intrusion of water if pump was located 0.3 meter under surface of oil.

(2) As above, but pump was located 0.1m under surface of oil.

(3) Pumping was performed using packer inside oil recovery well.

PROSPECTS FOR ROBOTICS IN HAZARDOUS WASTE MANAGEMENT

James F. Osborn, William L. Whittaker and Syd Coppersmith
Field Robotics Center
The Robotics Institute
Carnegie Mellon University
Pittsburgh, PA 15213

ABSTRACT

Robotic technology can provide solutions to some hazardous waste management problems. This paper discusses the intersection between automation technology -- already used in nuclear, subsea, mining, and other hazardous settings -- and candidate assessment and remediation tasks. First, robots are defined and classified according to complexity of the machine, environment, and task. Next, an overview is given of existing and emerging robotic technologies relevant to hazardous waste management. Possible near-term implementations using mature technologies are presented through the examples of site perimeter monitoring and chemical munitions disposal. The paper concludes with speculations on the future of robotics in hazardous waste management.

Introduction

Robotic technology holds the promise to provide unique, long-term solutions to a class of hazardous waste problems, but has not yet been introduced to this field. Advantages offered by robotics include eliminating the need for human presence in hazardous environments, robot capabilities beyond those of man (scale, forcefulness, sensing modes and computational ability), and the quality assurance and productivity of automation. Regulatory agencies, site operators and, most importantly, the public all stand to benefit by exploiting these advantages.

Robotic technology is not justified, either in terms of need or cost, for many hazardous waste management problems. Most "hazardous waste sites" do not pose acute hazard, the immediate threat to human life that is an irrefutable argument for robotic substitutes. Further, because of the current state of robotic technology, and given the cost of automation, many tasks in hazardous waste management are better performed by humans.

There is, however, a class of problems that urgent need and existing technology make viable candidates for robotic applications. These include tasks too hazardous for humans to perform, such as handling of nerve gas, radioactive waste or other severely toxic substances. Reducing human presence in such operations is imperative because it is impossible to adequately protect workers [1]. Capable robotic systems able to perform multiple functions, operate tools, and work for extended periods offer a viable alternative since they are relatively impervious to these hazardous environments.

Site characterization and long-term monitoring also present problems for which robotic technology offers solutions. Many sites are still incompletely characterized; for others there is a need to verify the confinement of the site contents during and after remedial activities. Proper assessment depends on repeated collection and analysis of consistent data in many forms. Through automation, these data can be acquired, processed, stored and correlated in greater quantities and at higher rates than possible using current methods.

Robot Attributes

Robots can be classified by several attributes: *control mode, degree of interaction with the environment, how well the task environment is structured,* and the *risks* associated with their actions [2]. Such classification lends insight to the match of robot technologies to particular tasks and environments.

In general, a robotic system consists of sensors to make measurements of phenomena in its environment, an actuator-driven mechanism to effect changes in this environment and a computing system which interprets sensor data, creates and instantiates models, generates plans and drives the actuators. The robot interprets sensory input to produce a model of itself and the world. Using this model, it specifies goals, formulates plans to achieve these goals, and executes the plans via control of the mechanism.

Robot *control modes* are defined by the split of responsibility for modeling, planning and initiating action among humans and computers. The simplest mode of robot control is teleoperation, where humans command actions through joysticks and other controls. A teleoperated robot may also be capable of performing simple reflexive functions (e.g., cessation of motion) based on raw sensor data to protect itself and its surroundings. For example, the Remote Work Vehicle (RWV), a teleoperated robot (Figure 1), performs nuclear cleanup tasks by remote control, but a bump sensor and electronic interlock prevent operators from raising its boom through an overhead obstacle [3].

At the other extreme of control, autonomy, the robot functions without reliance on a human operator. Using sensor data, the robot creates a semantic model of the world that it uses to plan its activities. These plans are decomposed into robot-executable commands and implemented without human intervention. REX (Figure 2), a robotic excavator, generates and uses such models and plans to uncover buried pipes. Data from sonar range sensors are used to construct terrain maps from which digging actions are commanded [4].

Intermediate between these levels is supervisory control, where the robot is commanded by an operator to perform tasks, but executes these tasks without reliance on the operator. The human supervisor interprets robot-constructed models (e.g., synthetic graphics) to generate directives for the robot. The Terregator (Figure 3), for example, uses its laser range finder to navigate through and map coal mines, but travel destination decisions are left to the supervisory operator [5].

Another way to classify robotic systems is by their *degree of interaction with the environment.* In non-invasive operations, such as inspection, mapping and air sampling, the robot and the world affect each other only slightly. For instance, the Remote Reconnaissance Vehicle (RRV) shown in Figure 4 observed the Three Mile Island Unit II reactor containment basement using video cameras and radiation detectors only. On the other hand, invasive operations like excavation, demolition and drilling alter the environment and occur by intimate coupling of the robot and its surroundings. An example of invasive robot interaction is the Remote Core Sampler

(Figure 5), which went beyond the RRV to cut concrete cylinders from the TMI basement walls using active tooling.

The applicability of a given robot to a particular task is governed largely by *how well the task environment is structured.* Factory robots perform repetitious tasks in an environment characterized by a consistent well-defined geometry. While this geometry might change, it does so in a deterministic manner that can be anticipated. Unstructured environments, in contrast, lack regular, obvious patterns that can be exploited for classification, recognition, and understanding. Consider the difference between a work station where an industrial manipulator is removing parts from a conveyor belt -- a repetitious task where the robot's superior repeatability provides better quality control -- and a field scattered with buried waste containers, where the robot's strategy for grasping each differs according to details of how the cannister lies and what immediately surrounds it. Robot interaction with an unstructured environment is dynamic (it evolves over time) and must be modeled through a process of incremental discovery and model refinement. Such environments defy preplanning and present the need to continuously manage contingencies.

The *risk* of robotic operations depends both on the nature of the task and on the capabilities of the robot. It is much riskier to handle cylinders of chemical munitions than it is to collect air samples from the perimeter of a hazardous waste site. There is little or no danger attendant to tasks of the latter variety, which are relatively non-invasive. As the strength of interaction between a robot and its environment increases, however, so does the risk of damage to the robot, its surroundings, or both.

Implicit in a robot's ability to accomplish is its ability to err. A large system deploying powerful tools, such as the Remote Work Vehicle (Figure 1), can inflict more damage than a system of lesser capability, such as the Remote Reconnaissance Vehicle (Figure 4). Risk is also associated with greater robot autonomy. As robots become increasingly self-reliant, they must cope with contingencies and tolerate faults that are potentially debilitating. Greater mechanical complexity and increased sensing and computation are required for less repetitive and less structured tasks, in conflict with the need for high reliability in unstructured environments.

Robotic Technologies for Hazardous Waste Management

Some robotic technologies applicable to hazardous waste management have reached a mature state while others are still in research or development stages. Mature technologies include locomotor and manipulator control, data acquisition, telemetry, power generation and distribution, electric motor technology, hydraulics, and man-machine interfaces. Current technology allows immediate implementations that approach simple tasks with simple control methods. More challenging applications will require the refinement of technologies that are not yet mature.

Developing technologies are advancing the state of the art toward robot autonomy, but are found predominantly in prototypes. Examples of these emerging technologies are machine perception, task planning, adaptive control and robust computing. As the cost of these technologies drops and capabilities improve, the viability of exploiting them increases. For example, the advent of inexpensive global positioning from navigation satellites makes feasible the guidance of mobile robots with higher accuracy and significantly less computation than is currently possible [6].

A developing technology essential to robotics is the integration of component technologies into complete systems. Robot integration is more subtle than bolting parts together: a system view of integration is necessary to arbitrate among subsystems competing for power, space and weight. The integration of unmanned systems must be more responsive than conventional equipment to such issues as task specificity, efficient modeling, operability, fault tolerance and reliability.

The defense and space industries are setting both the direction and pace of component technology development for new implementations. Many technologies are being driven in a programmatic manner: heavy resources are brought to bear on the computing, sensing and controls fundamental to systems of the future. The Strategic Defense Initiative and space station are good examples of this approach. Hazardous waste management currently provides less of a driving force to core robotics research and development, but provides an opportunity to integrate mature technologies for near-term robotic applications.

Example Applications of Robotics in Hazardous Waste Management

We speculate on site perimeter monitoring and chemical munitions disposal as hazardous waste management activities that are reasonable candidates for robotization. These are chosen on the basis of their technical viability, economic justification, and because they illustrate opposite ends of the robot attribute spectrum as set forth in the preceding section (see Table 1).

Site Perimeter Air Sampling

There is a legal mandate to protect the public from emissions of volatile organic compounds buried in hazardous waste sites [7]. This is necessary during remedial activities to warn of acute exposure and must continue in the ensuing years as an indicator of potential chronic exposure. Current methods for these assessments rely on multiple samplers of limited capability in fixed locations on the site periphery and manual transfer of these samples to laboratories for analysis. This assessment mechanism is sub-optimal because

Table 1. Attributes of Two Example Applications of Robotics in Hazardous Waste Management

Attribute	Site Perimeter Air Sampling	Chemical Munitions Disposal
Control mode	supervisory	teleoperated
Degree of interaction with the environment	non-invasive	invasive
Task environment	relatively structured	unstructured
Task performance	repetitive	each action unique
Risk associated with actions	low	very high

the expense of a capable distributed sampling system cannot be justified, and the logistics and cost of laboratory analyses limit the quantity of available data.

As an alternative, a mobile robot can make appointed rounds and implement perimeter monitoring protocols with advantages beyond traditional methods. Use of a single very capable device rather than a larger number of simpler fixed devices makes it possible to justify the purchase of more sophisticated sampling equipment, such as recently developed portable gas chromatographs and mass spectrophotometers [8]. A complete sample analysis that would, by present methods, take days or weeks could be performed in near real-time and a much greater quantity of data would be made available. The information would exhibit less variability, since all samples would be treated in a standardized fashion.

We envision a moderate terrain locomotor powered by a combination of batteries and a propane generator that slowly travels along the site fenceline using a position-based navigation system. Its course would be preprogrammed and maintained with an inertial navigation system, possibly with absolute positioning corrections from a number of robot-identifiable fixed landmarks. Soft bump detection, either by acoustic or laser scanning rangefinders, would be necessary to safeguard the robot from unexpected obstacles in its path. A two-way radio or cellular telephone data link would be used to send navigation and sampling instructions to the robot and receive data from the robot or serve as the telemetry system should teleoperation become necessary for setup, contingencies or service.

A relevant perimeter monitoring system would place few demands on site infrastructure. It would be hardened for multi-hour day/night operation in extremes of heat, cold, and precipitation. The system would incorporate bump detection and self-monitoring sensors to prevent damage to itself, the site and human attendants.

The site perimeter air sampling robot is a good example of a non-invasive robotic system. To be successful, it would maintain a minimal presence on the site, needing human attention only to alter sampling instructions or to replenish its power system. Sampling while slowly traveling along a predetermined course is a repetitive structured task with low associated risk. This risk is further reduced by outfitting the robot with proper safeguards.

Disposal of Chemical Munitions

The military must dispose of cannisters containing obsolete chemical agents stored in underground magazines or "igloos" at eight sites around the United States [9]. This is an extreme hazard, both in terms of exposure to cleanup personnel and the danger of accidental release as a result of remedial activities. The scenario is similar to the nuclear environment: human presence is precluded, the work space must be sealed during all operations, the environment is unstructured, tasks are non-repetitive and risks are great.

Remote operations are easily justified in this case by the risk of human exposure to the munitions. Robots would be unaffected by the large doses of these chemicals received during the years needed to complete this task. Safety considerations will force the cautious deliberate actions characteristic of teleoperated robots. We thus view that a mobile teleoperated work system is an ideal match to the problems associated with the decommissioning of chemical munitions facilities.

Such a system would follow the precedents set by nuclear work systems that perform similar missions with analogous constraints. It would feature at least one manipulator that is directly driven by, or "slaved to", a miniature replica, or "master", from a remote location and enhanced with force feedback from slave to master. The mobile base carrying the manipulator(s) would benefit from omnidirectionality, as the igloo interiors are cramped workspaces. Additional payload would include multiple video cameras and lighting, microphones, specific chemical detectors and system status sensors. The feedback of data and transmission of control signals to and from the operator control station would be via a multiconductor tether, which would likely carry primary power to the vehicle as well.

Beyond functional capabilities, a chemical disposal robot must be responsive to task environment and operational concerns. Attention must be paid to seals and surface finishes so that the robot can be effectively decontaminated following exposure. The system must also exhibit extreme reliability, since a robot that fails inside an igloo becomes part of the problem rather than providing a solution. Reliable cannister handling is a major consideration since rupture or chemical release are consequences of failure.

The high penalty for mistakes when handling chemical munitions is an example of the risk associated with highly invasive robot actions. This task environment is unstructured and a unique set of actions is used to handle each cannister. The complexity of this task mandates teleoperation, with human decision-making operative at all but the lowest level of control.

The above perspectives merely speculate on the intersection of needs in hazardous waste management and component robotic technologies. The example integrations, however, can be implemented in the near-term since they incorporate technologies that are or will soon be available.

Conclusion

Robotics for hazardous waste management is a fledgling discipline. It is too early to predict the role that robots will play or chart a direct path to that involvement. While there is a pressing need for pioneers to apply robotic technologies to the comprehensive needs of the hazardous waste industry, it is not apparent what technologies or applications will be successful. Performance is perhaps the best measure of relevance: robotic applications will be judged not only by capability, but also by cost, availability, and reliability.

Formative integration must ultimately come from the hazardous waste management industry itself. It is essential that the industry identify and drive the developments that will distinguish hazardous waste robotics as a discipline in its own right. There is now a unique opportunity to exploit the intersection between robotic technologies and the hazardous waste need. Just as it is important to remain open and flexible to emerging capabilities and problems, it is imperative to seek early implementations and the insights that only experience can provide.

References

1. Levine, S.P. and W.F. Martin, Protecting Personnel at Hazardous Waste Sites, Butterworth Publishers, Boston, MA, 1985.

2. Whittaker, W.L., "Construction Robotics: A Perspective," International Joint Conference on CAD & Robotics in Architecture and Construction, Marseilles, June 1986.

3. Whittaker, W. L. and L.E. Champeny, "Capabilities of a Remote Work Vehicle," Topical Meeting on Robotics and Remote Handling in Hostile Environments, American Nuclear Society, Seattle, March 1987.

4. Whittaker, W.L. and B. Motazed, "Evolution of a Robotic Excavator," International Joint Conference on CAD & Robotics in Architecture and Construction, Marseilles, June 1986.

5. Whittaker, W.L., G. Turkiyyah, and M. Hebert, "An Architecture and Two Cases in Range-Based Modeling and Planning," Proceedings of the IEEE International Conference on Robotics and Automation, Raleigh, April 1987.

6. Collins, J. "GPS Equipment Survey," Point of Beginning, Vol. 12, pp. 11-22, 1987.

7. U.S. Environmental Protection Agency (1980, 1981). *Ambient Monitoring Guidelines for Prevention of Significant Deterioration,* Report EPA-450/4-80-012. U.S. Environmental Protection Agency, Offices of Air Quality Planning and Standards and Research and Development, Research Triangle Park, NC.

8. Puskar, M.A. and S.P. Levine, "Characterization of Bulk Materials on Remedial Action Sites: A Preliminary Comparison of Compatibility Testing, FT-IR and GC/MS," Proceedings of the National Conference on Hazardous Waste and Environmental Emergencies, May 1985.

9. U.S. Army Toxic and Hazardous Materials Agency, "Chemical Stockpile Disposal Program," Aberdeen Proving Ground, MD, 1987.

Disclaimer

The work in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

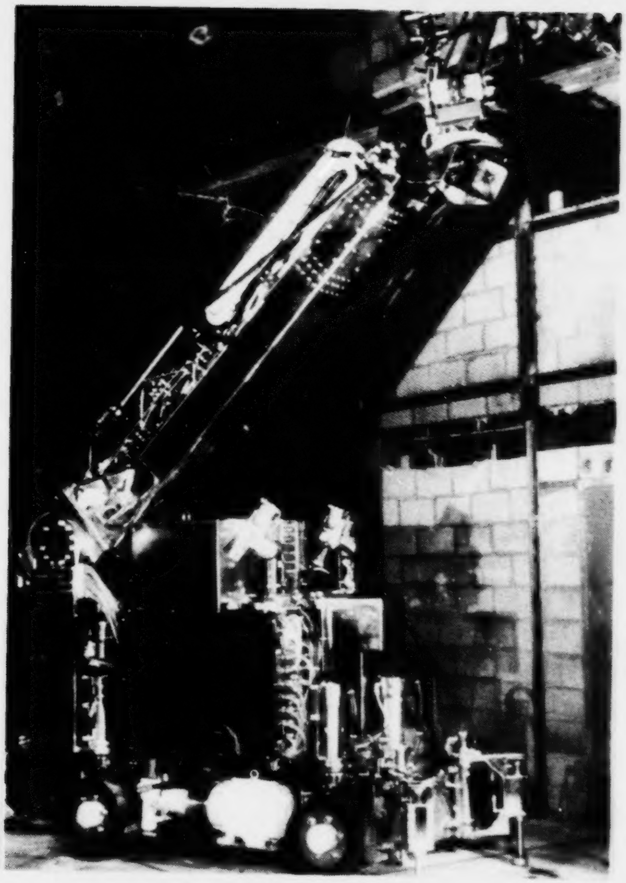


Figure 1. The RWV is a teleoperated robotic work system for nuclear environments.

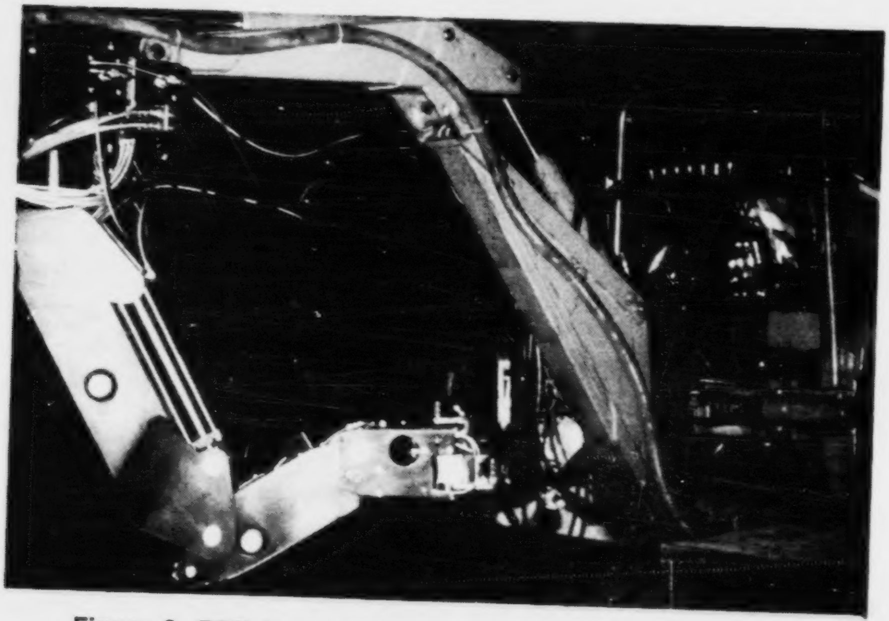


Figure 2. REX is an autonomous robot for excavation.

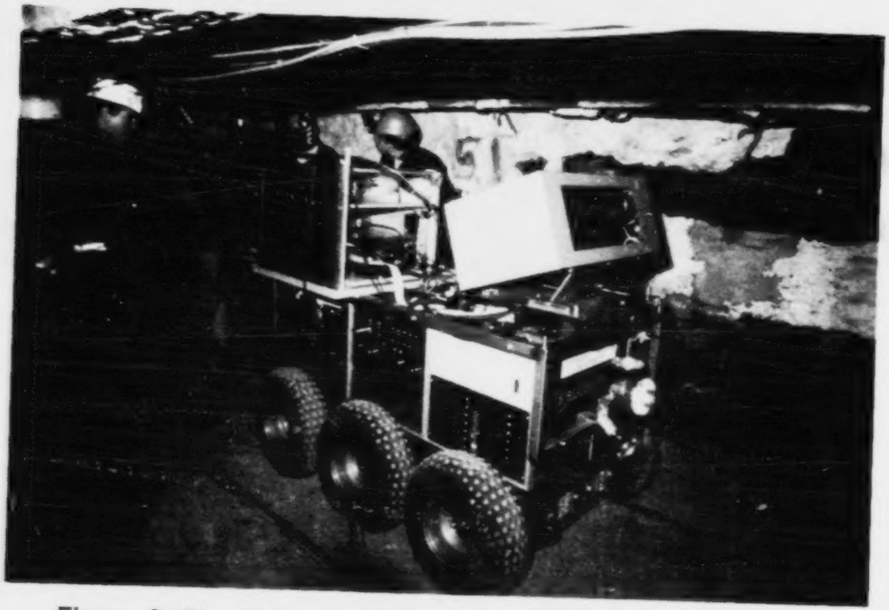


Figure 3. The Terregator can navigate a coal mine under supervisory control.

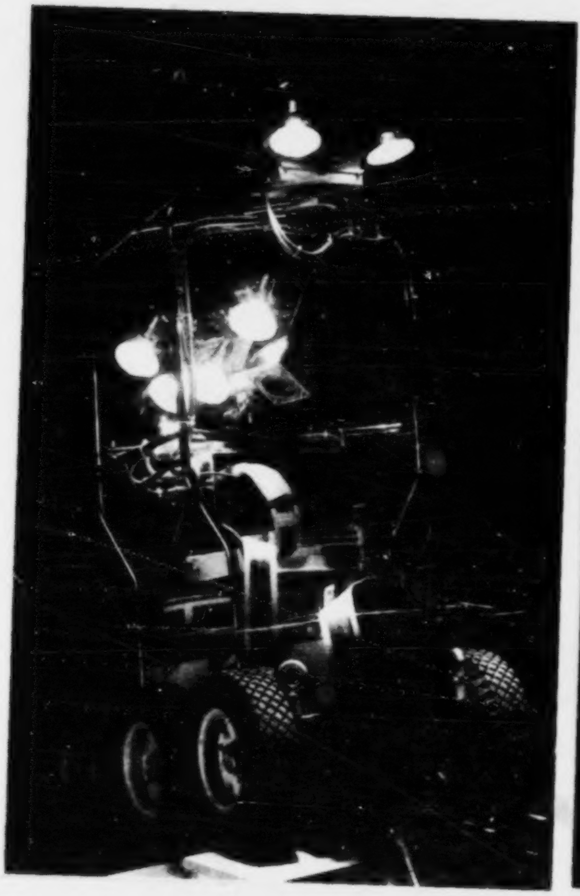


Figure 4. The RRV provided the first views of the TMI Unit II reactor containment basement following the 1979 accident.

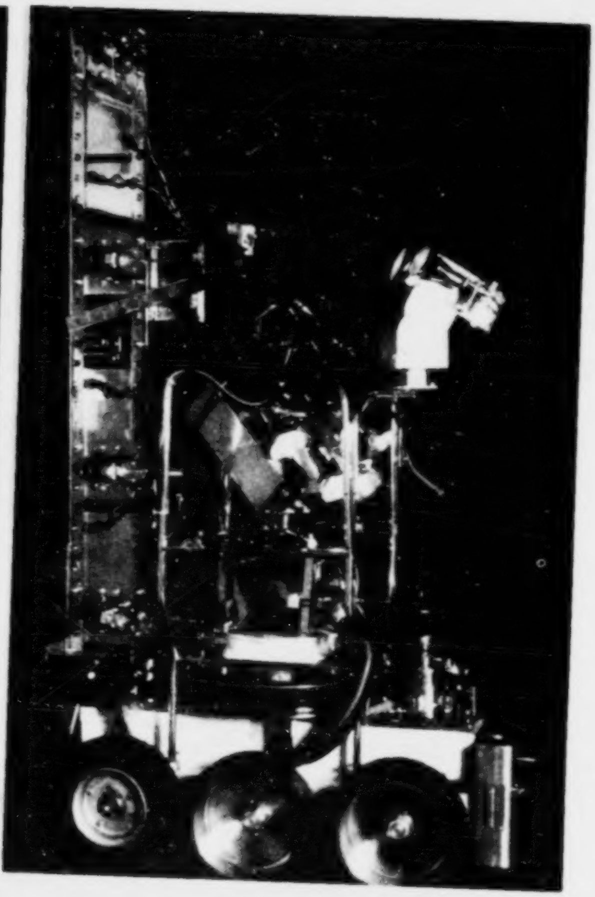


Figure 5. The Remote Core Sampler used electrohydraulic drills to remove concrete samples from the basement walls.

EVALUATION OF AN ENGINEERED BIODEGRADATION LAND TREATMENT SYSTEM FOR SOIL DECONTAMINATION AT A WOOD PRESERVING SITE

Jaw K. Fu and John R. Smith

KEYSTONE ENVIRONMENTAL RESOURCES, INC.
Monreville, PA

ABSTRACT

To evaluate Engineered Biodegradation System (EBDS^{TM}) treatment of soil contaminated with creosote and PCP wood preservative residues at a former wood treating site, an engineered field treatment plot was constructed and loaded with contaminated soil for susequent treatment. The treatment area was approximately one-quarter acre in size and was loaded with approximately 600 tons of contaminated soil. Stormwater run-off and run-on was controlled by surface grading and stormwater retention basin. Normal operation of the unit entails moisture control, pH control, nutrient addition, and periodic tilling. The unit was operated during a six-month period from May through October in 1986. During this time period, sampling and analysis of the air, surface soil, subsurface soil, and the groundwater, was carried out to address chemical reduction, chemical migration, air emissions, groundwater impact, and acute toxicity reduction.

This paper presents the proceedures and results of an ongoing field investigation evaluating EBDS as a unit process that treats organically contaminated soil utilizing the capacity and the soil matrix to biodegrade and immobilize the contaminants of concern. EBDS is an aerobic soil mixture approximately 0.5 to 1.5 feet deep that is managed to promote the growth of indigenous microorganisms to biodegrade contaminants and to promote immobilization of contaminants. The EBDS design combines: (i) engineering expertise, (ii) risk management, and (iii) regulatory liaison.

The results of the work supported that EBDS is a very effective means to treat soil contaminated with PCP and cresote components for the site studied. Specifically, the results showed that:

(i) Chemical/biological transformations accounted for over 80 percent of PCP removal and over 90 percent of PAH removal;

(ii) decomposition products were determined to be nontoxic by both microtox and daphnia acute toxicity assays;

(iii) air emission monitoring showed volatilization of approximately 0.1 percent to 15 percent of naphthalene and some noncarcino-

genic PAHs and less than 0.1 percent of PCP and carcinogenic PAHs;

(iv) PCP, naphthalene, and PAHs were not detected in the soil below the zone of incorporation;

(v) TCLP leaching tests at the end of the six-month treating cycle resulted in nondetectable levels of PCP and PAHs, and

(vi) November groundwater monitoring results at the end of the six-month treating cycle showed no detectable levels of PCP and PAHs resulting from EBDS treating cell.

Ongoing work with the same field demonstration plot continues through this year evaluating the effect of a second year of contaminated soil application and treatment.

****

WHERE ENTIRE PAPER HAS NOT BEEN INCLUDED IN THESE PROCEEDINGS COPIES WILL BE AVAILABLE IN THE CONFERENCE LOBBY.

STIMULATION OF MICROBIAL BIODEGRADATION IN A JET FUEL CONTAMINATED SOIL

Raymond N. Yong, Diana Mourato
Geotechnical Research Centre
McGill University, Montreal
Quebec, H3A 2K6

ABSTRACT

Previous studies have indicated the marked effect of aeration and nutrient additions on the ability of indigenous soil microbial populations to biodegrade intruding organic contaminants. A similar phenomenon was utilized in this study for enhancing the biodegradation of jet fuel contaminated soils through stimulation of the soil's indigenous microorganisms. This study was carried out as a preliminary investigation to establish the necessity to develop in-situ aeration technology.

Jet fuel biodegradation was enhanced by supplying air, nitrogen, phosphorus and trace minerals to the contaminated field soils. Jet fuel biodegradation was monitored by CO_2 evolution and by following hydrocarbon transformation through gas chromatography and infra-red spectroscopy studies.

Comparative studies were conducted between aerated and non-aerated soils. Whilst aeration was observed to significantly enhance CO_2 evolution and hydrocarbon degradation, non-aerated soils have also displayed some jet fuel biodegradation. The rates of CO_2 evolution and hydrocarbon degradation were shown to be significantly slower in the non-aerated soils, whereas the addition of external sources of nitrogen and phosphorus was more important for degradation to occur. Jet fuel degradation was only initiated after a lag time in the non-exposed soils, whereas the contaminated soils showed immediate response. This phenomenon appeared to be related to the presence of jet fuel adapted microbial species within the soils which have been contaminated for a period of 5 to 10 years.

INTRODUCTION

Contamination of soils and groundwater with hydrocarbon products is a concern of environmentalists since petroleum products are toxic compounds known to be harmful to aquatic life at concentrations equivalent to 90 ppm (1). The problem of leaking buried gasoline tanks as sources of groundwater contamination is indeed a real and pressing issue.

Contaminated soils could either be excavated, displaced and treated, or treated in-situ. There are advantages and disadvantages in all cases but for large volumes of contaminated soils, in-situ detoxification / decontamination is an alternative to be considered. If so, techniques of land-farming used for oily sludges become applicable.

Gasoline products are composed of a variety of aromatic hydrocarbons. Common gas hydrocarbons comprise toluene, xylene, benzene, ethyl benzene, intermediary hydrocarbons, etc. The aromaticity of these hydrocarbons renders biodegradation a more difficult task, but partial degradation of such compounds under aerobic conditions in soils has been referenced (2, 3). Hydrocarbons are known to be biodegraded by a variety of bacterial species. Low molecular weight aromatic hydrocarbons, in particular, have been observed to undergo significant biodegradation under aerobic conditions (3, 4). In contrast, anaerobic biodegradation of aromatic hydrocarbons has been largely discounted over the years. More recent studies have, however, shown hope for anaerobic biodegradation of polyaromatic hydrocarbons, although an equivalent concentration of these compounds were shown to be biodegraded more than 20 times as rapidly under aerobic conditions, with a lag time for initiation of anaerobic biodegradation of more than 270 days (3, 4).

PURPOSE

Initially, the studies reported herein were conducted as a preliminary investigation to establish the usefulness of soil aeration for in-situ soil decontamination of an actual jet fuel contaminated site. Results have, however, shown that although aerobic treatment was faster and more efficient, anaerobic biodegradation appeared to occur, and this could be enhanced through enrichment of the soils with non-carboneous nutrients. The objectives of this study included gaining a better understanding of natural soil-related phenomena available for in-situ biodegradation (and possibly reactor biotechnology) of hydrocarbon-contaminated soils, and evaluating metabolic stimulation procedures for further field application.

This paper summarizes studies conducted to evaluate the ability of soils to undergo self-decontamination under aerated and non-aerated conditions. More precisely, emphasis was put on the influence of soil microbial activity on the decontamination process. Enhanced hydrocarbon degradation and microbial activity are studied through aeration and supply of non-carbonaceous co-nutrients to soils exposed to the contaminant for a period of 5 to 10 years and to soils which have not been previously exposed to hydrocarbons.

APPROACH

Two main experiments were conducted; namely a jet fuel-contaminated soil biodegradation assay, and an adaptability assay.

Soils: The contaminated soils sampled consisted of a mixture of gravel and silt (fill material), contaminated with jet fuel that has overflowed from reservoirs over the last 5 to 10 years. The soil's hydrocarbon content was shown to be equivalent to 5% w/w and water content of 10%.

A laboratory processed soil, consisting primarily of illitic minerals with some chlorite and kaolinite, was used for the adaptability studies.

Biodegradability assay: 320g of jet fuel contaminated soils (5% w/w jet fuel) were continuously aerated with CO_2-free compressed air, routed to a manifold system which distributed air to the culture vessels (refer to Fig. 1). Gas flow did no induce soil mixing in the vessels. The soils were not inoculated for the test and any detected microbial activity was considered to be inherent to the soil. The CO_2 produced in the vessels could originate from two sources; chemical or biological processes. Although chemical oxidation of the hydrocarbons has to be considered, biodegradation appeared to be the most important generator of carbon dioxide.

Non-aerated reference tests were carried out in parallel by replacing the flowing air with argon. These soils were initially purged with argon to evacuate trapped oxygen. Non-aerated conditions were ensured by maintaining a positive argon flow throughout the duration of the test. Air evacuation was monitored with a Yellow Springs oxygen meter and an oxygen-free environment was insured throughout the test, by incorporating a Gas Pack disposable anaerobic indicator in each vessel. These provided visual evidence that anoxic conditions were maintained.

All soils were enriched at various stages with minimal salts solution (20mL in 320g), consisting of the following constituents:

20g/L NH_4Cl
4g/L HN_4NO_3
8g/L Na_2SO_4
4g/L KH_2PO_4
0.4g/L $MgSO_4$
12g/L K_2HPO_4

These salts could offer sources of exogenous electron acceptors, susceptible to induce oxygen-free hydrocarbon oxidation and produce carbon dioxide. This had to be taken in account in the interpretation of the CO_2 evolution curves.

To follow hydrocarbon transformation, two types of tests were conducted; gas chromatography of pore fluid extracts and infra-red spectroscopy of air-dried soils. Stripping of hydrocarbons had to be considered as a small contribution to hydrocarbon disappearance and was considered in the analysis of the results.

CO_2 evolution was monitored by 2 distinct tests:

- Barium hydroxide
  ($Ba(OH)_2$ - CO_2 trapping).

Carbon dioxide produced within the reaction vessels was directed towards a series of 125 mL flasks containing 100 mL of 0.024N $Ba(OH)_2.8H_2O$ (refer to Fig. 1). The carbon dioxide contained in the flowing gas was trapped by $Ba(OH)_2$ in the form of $BaCO_3$. The cumulated CO_2 trapped as $BaCO_3$ was determined daily in the 2 flasks by titration of the absorbers with 0.05N HCl to a phenolphthalein end-point. The amount of carbon dioxide produced in a given time period was calculated as follows (5);

CO_2=0.025 mole/mL x vol HCl x 44 mg CO_2

- CO_2 analysis by infra-red detection.

At irregular time intervals, the gas tube leading to the $Ba(OH)_2$ flasks was diverted to an infra-red detector, part of a Beckman - Total Organic Carbon Analyzer IR detector, model 915. The CO_2 contained in the gas flowing from the soils represented the CO_2 produced within the material, by chemical or biological reactions.

Jet fuel analysis, before and after the incubation periods, was performed using the following methods:

- Gas chromatography by flame ionization detection (FID)

2 microliter samples of acetone extracted pore fluid samples, were injected in a 10% OV-351 Chromosorb W-HP 80/100, 20ft column. Carrier gas (Helium) was set at a flow equivalent to 25 mL/min. Hydrocarbon analysis was carried out by means of a temperature program set as follows:

initial: 100°C for 4 mins.
program: 4°C/min
final: 150°C for 8 mins.

- Infra-red spectroscopy (Beckman Acculab 9)

IR analysis was carried out in a 4000 to 300 cm^{-1} wavelength range. 5 mg air dried soil samples were mixed with 495 mg dried KBr, finely ground and pressed into a pellet. IR spectra were analyzed as a function of new peaks related to the soil or to the contaminating hydrocarbons.

Adaptability assay: These assays were carried out to investigate the potential of non-exposed soils to undergo hydrocarbon biodegradation in aerated and non-aerated conditions. Due to their nature, the adaptability tests allowed to study the initial steps of jet fuel biodegradation, since non-degraded jet fuel was admixed to non-exposed soils. In contrast, the biodegradability tests were conducted on contaminated soils in which in-situ biodegradation has been initiated. The adaptability assays compared CO_2 evolution and hydrocarbon biodegradation of aerated and non-aerated soils inoculated with microbes never before exposed to hydrocarbons.

The adaptability tests set-up (gas distribution and analysis) was similar to the biodegradation assays' set-up described above, but the tests were conducted on laboratory processed sterile soils (Domtar Sealbond soils), enriched with 50 mL jet fuel and 50 mL minimal salts solution, and specifically inoculated with 20g hydrocarbon-free top soil.

During the test period, CO_2 evolution was monitored by both $Ba(OH)_2$ and IR analysis. After 13 days of incubation residual jet fuel in the soils was analyzed by IR and GC tests. Comparisons were established between aerated and argonated assays in both natural and reference soils. Control samples consisted of jet fuel-free inoculated Domtar Sealbond soil and sterile jet-fuel enriched soils (to investigate evaporation effects).

RESULTS:

Carbon dioxide Evolution
Biodegradability assays:

Both CO_2 evolution tests suggested that CO_2 was produced in all soils, but the rate at which CO_2 was synthesized varied in accordance with the treatment given. Aerated soils were characterized by elevated CO_2 evolution curves, whereas non-aerated soils had carbon dioxide levels of approximately half (refer to Figures 2 and 3). This was verified in both cumulative tests (by $BaCO_3$ titration) and by direct CO_2 analysis (IR spectroscopy).

It has only been recently that studies have indicated the existence of a slow anaerobic catabolism of hydrocarbons. In all cases, however, anaerobic hydrocarbon catabolism only starts after a long period of time (270 days) (3, 4). This long adaptation time was not reflected in our experiments, but could have occurred naturally over the years at the site. The CO_2 evolution curves do not represent the activity of microbes recently in contact with the pollutant, but of microbes which had more than 5 years to adapt to the fuel.

Whilst CO_2 evolution is an acceptable tool to investigate metabolism, care needs to be exercised in the interpretation of results - especially in relation to biodegradation of pollutants. Depending on the pathway taken to catabolize the contaminant, the reaction stochiometry will differ and the microbes will produce different quantities of carbon dioxide. Also, depending whether mineralization of cellular synthesis occurs, the ratio of CO_2 produced will be different. Finally, as mentioned above, carbon dioxide can also be produced as a result of chemical oxidation. For these reasons, CO_2 evolution curves were interpreted in view of the results generated by GC and IR tests.

Carbon dioxide evolution was used to evaluate the influence of minimal salts on both aerated and non-aerated soils. Both soils exhibited large increases in CO_2 production after addition of these co-nutrients (refer to Figure 5). Addition of salts could result in an increase in chemical oxidation and CO_2 evolution, even in the absence of oxygen, since the salts can supply electron acceptors. Nevertheless, results derived from the adaptability studies confirmed that this phenomenon was limited in the tests, and the measured CO_2 could be indeed related to biological activity. The influence of salts reflected the lack of non-carbon nutrients in hydrocarbon rich soils, often a limitation for biodegradation to occur. This agrees with studies conducted on oil biodegradation in soils (6, 7).

Carbon dioxide was also used for rapid screening of the nature of the metabolizing microbes. To assess whether the microbes in the non-aerated soils were strict anaerobes, the non-aerated soils were aerated for a period equivalent to 10 days after 30 days of non-aerated treatment. In all cases, the CO_2 produced was significantly enhanced after the first day (no lag time) (refer to Fig. 4).

Interpretation of these results could be made on the basis of a chemical oxidation phenomenon. Nevertheless, the results seem to indicate that the metabolizing microbes were not sensitive to air, unless the activity detected was attributed to fast growing aerobes. This in turn suggests that the microbes were most probably facultative anaerobes undergoing anaerobic respiration. Biodegradation of hydrocarbons by facultative microbes through anaerobic respiration, utilizing nitrogen and/or sulfate as a final electron acceptor has also been demonstrated by other researchers (8, 9).

Carbon dioxide Evolution Adaptability assays:

Carbon dioxide evolution of the soil samples undergoing adaptability tests were similar to the ones presented for biodegradation studies (refer to Figs. 4 and 5). In summary, the non-aerated samples exhibited some carbon dioxide production, but this was significantly lower than the aerated soil samples. However, these results could not be interpreted without the support of GC and IR results, since the observed carbon dioxide synthesized could originate from the biodegradation of non-hydrocarbon organics present in laboratory soil or added in the inoculum.

Gas chromatography Biodegradability assays

Gas chromatography of the non-treated jet fuel revealed a large number of peaks related to the hydrocarbons present in the fuel (Fig. 6, curve a). No attempt was made to identify all hydrocarbons, but the dominating peaks (f, j and p) were identified as being benzene, toluene and xylene peaks respectively; 3 major compounds of jet fuel. Furthermore, analysis of the jet fuel chromatograms emphasized the high molecular weight nature of some of the fuel constituents.

Over the years, in-situ, natural biodegradation appeared to have taken place, transforming the jet fuel into a product of decomposition. However, the periodic addition of fresh jet fuel resulting from continuous spills would indicate that the sampled soils could contain jet fuel at different states of degradation. This was indeed exhibited by a chromatogram of the soil's pore fluid (Fig. 6, curve a). Comparative analysis of the jet fuel and of this pore fluid extract suggests that in-situ natural biodegradation had indeed taken place, eliminating most low molecular weight hydrocarbon peaks. The presence of toluene, xylene and a compound with similar molecular weight as xylene (peak o') (absent in the original jet fuel) is, however, noticeable. The results indicate that natural biodegradation is more effective in degrading the low molecular weight hydrocarbons, in accord with the results reported by Atlas (4).

As expected, biodegradation resulted in the appearance of an important number of peaks in the non-aromatic area of the chromatogram (first peaks to appear). These low molecular weight compounds would consist of by-products of biodegradation since the original jet fuel only exhibited insignificant peaks in this chromatogram region. Similar results were reported for chromatography studies of biodegraded hydrocarbons (10, 11).

Non-aerated laboratory treated soils exhibited pore fluid chromatograms very similar to the field extract. However, the intensity of high molecular weight compounds' peaks were reduced whereas the low molecular weight compound peaks exhibited increased intensity. Furthermore, the o' peak seen in the in-situ soil's pore fluid extract was also clearly shown in these chromatograms. Overall, these results supported the CO_2 evolution curves by demonstrating that even without aeration, biodegradation was successfully continued with the introduction of low concentrations of nitrogen and phosphorus in the system.

Aeration of the nutrient-enriched contaminated soils for a period of 30 days appeared to significantly reduce the presence of higher molecular weight compounds while building up a reserve of low molecular weight by-products of biodegradation (Fig. 6, curve c, peaks a, b, c and f). As had been noted previously, catechol, acetyl-COa, succinate, acetaldehyde and pyruvate are common by-products of biodegradation of aromatic hydrocarbons and their synthesis depends on the metabolic pathway taken (4). These by-products are all of lower molecular weight than most hydrocarbons present in the jet fuel, and their synthesis would appear on the chromatograms as peaks with short retention times (eg. peaks a to e). Further studies are presently being conducted to identify and compare by-products from aerated and non-aerated soils.

Also of interest was the disappearance of peak o' (possibly a by-product of biodegradation), in the aerated soils. Development of equivalent peaks in the low molecular range seems to indicate that aeration is required to biodegrade the component related to this o'peak. It would appear that catabolism of the jet fuel could also be due to the anaerobic respiration of facultative microorganisms present in the soils. It would appear that oxygen is required to fully biodegrade the element related to the peak o'.

Gas Chromatography Adaptability assays

The results shown in Figure 7 indicate that in general larger reductions in peak heights were obtained in the aerated samples, confirming the CO_2 evolution results. The following points are noted:

- whilst similar trends were observed in the chromatograms, the peak intensities of non-aerated soils were higher than in the aerated soils.
- in the incubation period of 13 days, the results indicate that only low molecular weight hydrocarbons were biodegraded in both aerated and non-aerated soils with a net decrease in the first peaks of the chromatogram.
- The j peak (toluene) in aerated soils was shown to be displaced to the left (shorter retention time). A study of the significance of this event has yet to be performed.
- the non-aerated soils' chromatograms indicated that the o' peak discussed above, and thought to be related to a by-product of anaerobic biodegradation, is formed after only 13 days of treatment under anaerobic conditions.

In summary, gas chromatography studies indicate that the CO_2 evolution observed is related to the biodegradation of non-aromatic low molecular weight compounds and probably to some short chain hydrocarbons, in non-aerated soils containing no adapted microbes. Furthermore, biodegradation appears to be accompanied by a build-up of an intermediary product common to the non-aerated soils (peak o').

However, aerated non-adapted microbes pre-sent in topsoils appear to exhibit some low and intermediate MW hydrocarbon biodegradation without build-up of the o' peak-related intermediary by-product.

IR spectroscopy
Biodegradability assay

The aerated and non-aerated spectra shown in Fig. 8 indicate the presence of absorption bands typical of both laboratory soil and jet fuel peaks (compare D and JF bands). However, the non-aerated spectrum shows a predominance of jet fuel bands (JF1, JF3 and JF4). These overshadow the presence of laboratory soil's characteristic bands (D4 (900 - 1100 cm^{-1} region)).

Only trace bands of jet fuel were noticeable in the aerated soils. One might conclude from these results that the contribution of air enhances jet fuel degradation. We note that these results support the CO_2 evolution data generated and discussed above. From IR spectroscopy one can also conclude that the actual source of CO_2 produced in this assay is the result of catabolism of jet fuel hydrocarbons.

IR spectroscopy
Adaptability assays:

Infra-red analysis of the soils derived from the adaptability assays (refer to Figure 9) lead to the same conclusions as above: The non-aerated soils exhibit IR absorption bands typical of both laboratory soil and the contaminating jet fuel (eg. peaks JF2, JF3, JF4 and JF5), whilst the bands from the aerated soils only reflect the soils' spectrum. Again, the jet fuel bands overshadowed the laboratory soil typical peaks in the 900 - 1100 cm^{-1} region in the non-aerated soils' IR spectrum. Since the adaptability tests were only run for 13 days, the state of degradation was less than in the biodegradability samples which were run for thirty days.

Conclusions and Applications

It would appear that it is possible for non-aerated field soils exposed for long periods of time to an aromatic hydrocarbon source (eg. jet fuel) to develop adapted microbial species that can use the contaminant as a source of carbon. The biodegradation rate would, however, be slower in comparison to aerobic catabolism. All hydrocarbons present would probably not be mineralized (especially the high MW molecules), and some by-products of biodegradation could accumulate in the soils. With an external addition of a source of readily available nitrogen and phosphorus to the soils, enhancement of CO_2 evolution and hydrocarbon degradation occurs (supported by both IR and GC results).

The results obtained indicate that the anaerobic biodegradation monitored could be partially attributed to facultative anaerobes undergoing anaerobic respiration. In the absence of oxygen, however, an intermediary by-product of biodegradation is shown to accumulate in the soil, and that for further degradation of the by-product, oxygen is probably required. Studies on accumulation and toxicity of the synthesized by-products, are presently being conducted.

In soils, not previously exposed to hydrocarbons, oleophilic microbes are not naturally present, and although some CO_2 evolution was observed, this can be related to the biodegradation of low molecular weight compounds of non-aromatic nature. Fresh hydrocarbon (jet fuel) spills in non-preconditioned anaerobic soils may not undergo self-decontamination even if large amounts of nitrogen and phosphorus nutrients are added, because of the absence of non-adapted microbial species. As indicated in this study, one could expect that given sufficient time, adapted microbial species can develop, therefore permitting slow biodegradation/decontamination to occur. Inoculation of the soil with adapted anaerobes, and a supply of additional nutrients, could also be a remediation solution technique to be considered if accelerated biodegradation is desired.

Aerated soils exhibited faster fuel biodegradation rates by both adapted and non-adapted soil microbes, with more complete hydrocarbon degradation. The results confirm the advantages of aerating contaminated soils, and suggest that development of aeration processes for soils would be a useful technology to implement for a faster and more thorough decontamination of soils. Incorporation of a mechanism to supply nitrogen and phosphorus solutions to the soil should allow for better treatment efficiency. Whilst aerobic biodegradation of hydrocarbons in-vitro has been well studied, field applications of aerated in-situ decontamination requires the development of proper technology.

Anaerobic in-situ treatment appears to be a relatively new subject. Laboratory investigations of metabolic enhancers including detailed studies to evaluate the influence of nitrogen, phosphorus and water content on biodegradation, steps of biodegradation, by-products of metabolism, and toxicity of these by-products need to be conducted. Development of such a technology would, however, be applicable to a variety of refractory contaminants which biodegradation could be enhanced by aeration of the soil.

ACKNOWLEDGEMENTS

The study was conducted under a Grant in aid of Research from the Natural Science and Engineering Research Council (NSERC) of Canada, Grant no. A-882. Special acknowledgement is due to R.D. Ludwig for his support and assistance.

REFERENCES

1- Environment Canada (1984) Manual for Spills of Hazardous Materials Environmental Protection Service. March 1984.

2- Bossert, I., Kachel, W.M., and Bartha, R. (1984) **Fate of Hydrocarbons during Oily Sludge Disposal in Soil**. Applied and Envir. Microbiol. 47:763-767.

3- Atlas, R.M. (1986) **Fate of Aromatics in the Environment**. Environmental Insult and Recovery of Stressed Systems Symposium. ASM-CSM Symposium. Toronto, Canada.

4- Atlas, R.M. (1981) **Microbial Degradation of Petroleum Hydrocarbons: an Environmental Perspective**. Microbiological Reviews. 45:180-209.

5- Larson, R.J. (1979) **Estimation of Biodegradation Potential of Xenobiotic Organic Chemicals**. Applied and Envir. Microbiol. 38:1153-1161.

6- Lehtomaki, M. and Niemela, S. (1975) **Improving Microbial Degradation of Oil in Soil**. Ambio. 4:126-129.

7- Dibble, J.T. and Bartha, R. (1979) Effect of Environmental Parameters on the Biodegradation of Oil Sludge. **Applied and Envir. Microbiol.** 37:729-739.

8- Bailey, C.A., Jobson, A.M and Rogers, M.A. (1973) **Bacterial Degradation of Crude Oil: comparison of field and experimental data**. Chem. Geol. 11:203-221.

9- Pierce, R.H., Cundell, A.M., and Traxler, R.W. (1975) **Applied Envir. Microbiol**. 29:646-652.

10- Smith, E.F. and Paulsen, K.E. (1985) **Petroleum and Petrochemical Analysis by Gas Chromatography**. in Grob, R.L. Modern Practice of Gas Chromatography. John Wiley and Sons, pages 631-719.

11- Bilstad, T., Bosdal, T and Toerneng, E. (1986) **Biodegradation of Oil on Drilled Cuttings**. IAWPRC 13th Biennial International Conf. proceedings. Rio De Janeiro, Brasil.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

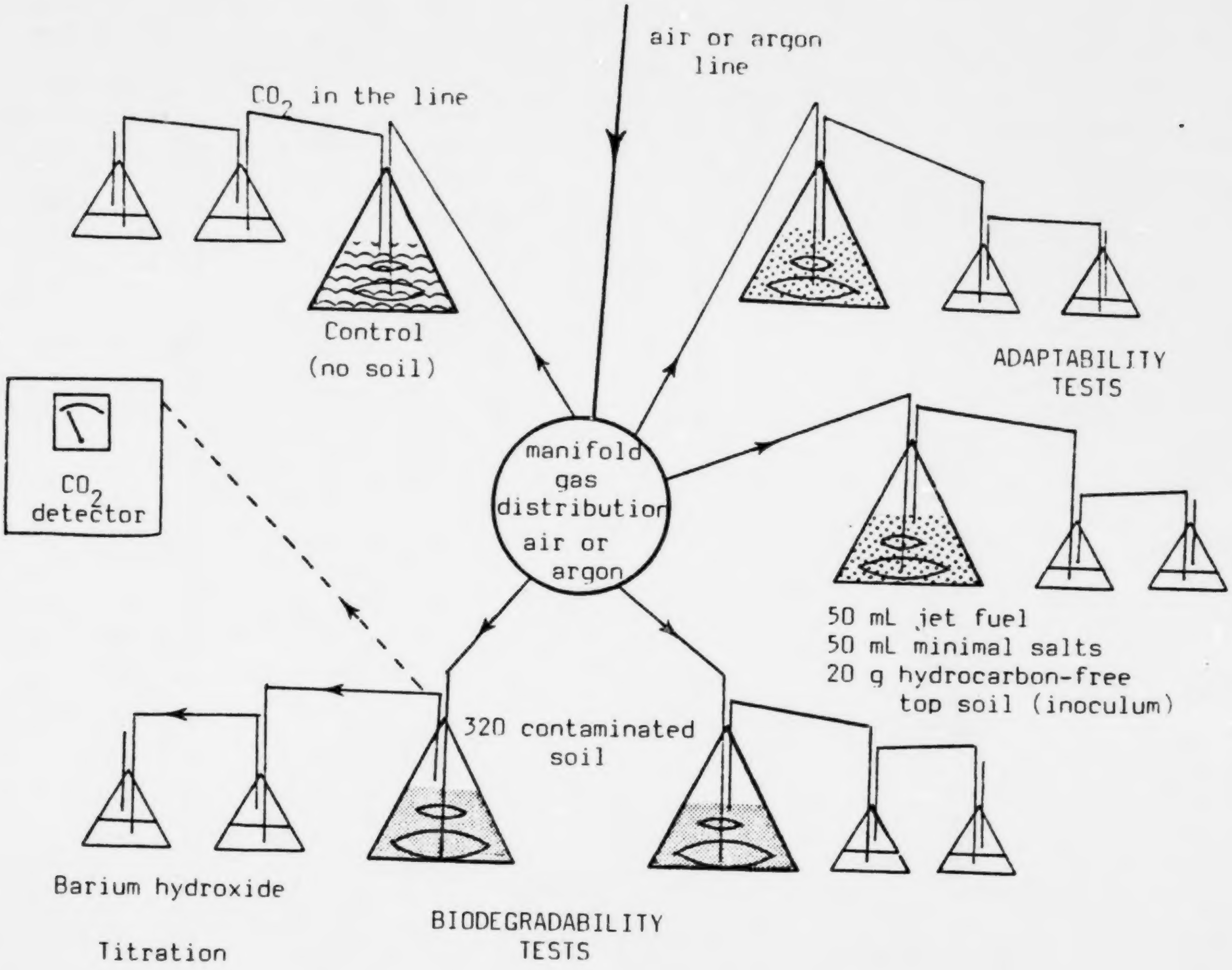

air or argon line
CO$_2$ in the line
Control
(no soil)
ADAPTABILITY TESTS
CO_2 detector
manifold gas distribution air or argon
50 mL jet fuel
50 mL minimal salts
20 g hydrocarbon-free top soil (inoculum)
320 contaminated soil
Barium hydroxide
Titration
BIODEGRADABILITY TESTS

Figure 1, Experimental set-up for the biodegradability and the adaptability assays.

Figure 2 BIODEGRADABILITY ASSAY
CUMULATIVE CO_2 CURVES

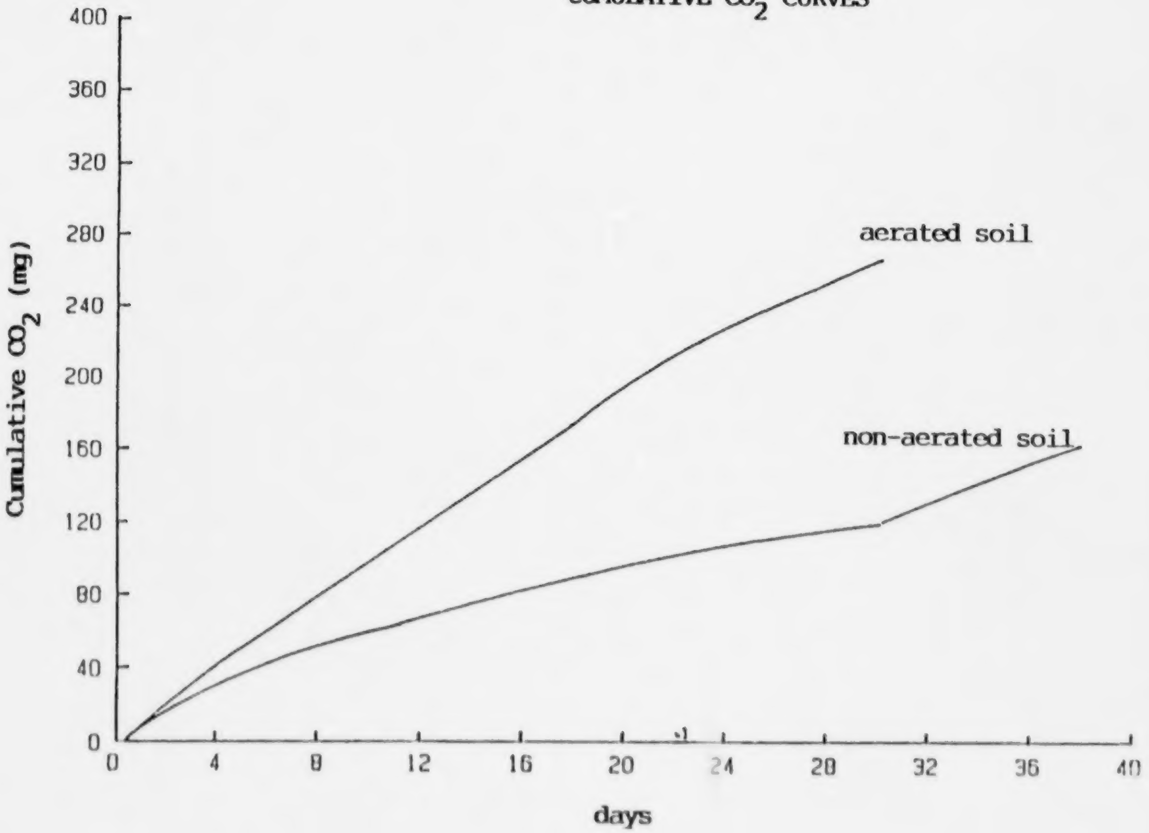


Figure 3 ADAPTABILITY ASSAY
Cumulative CO_2 Curves

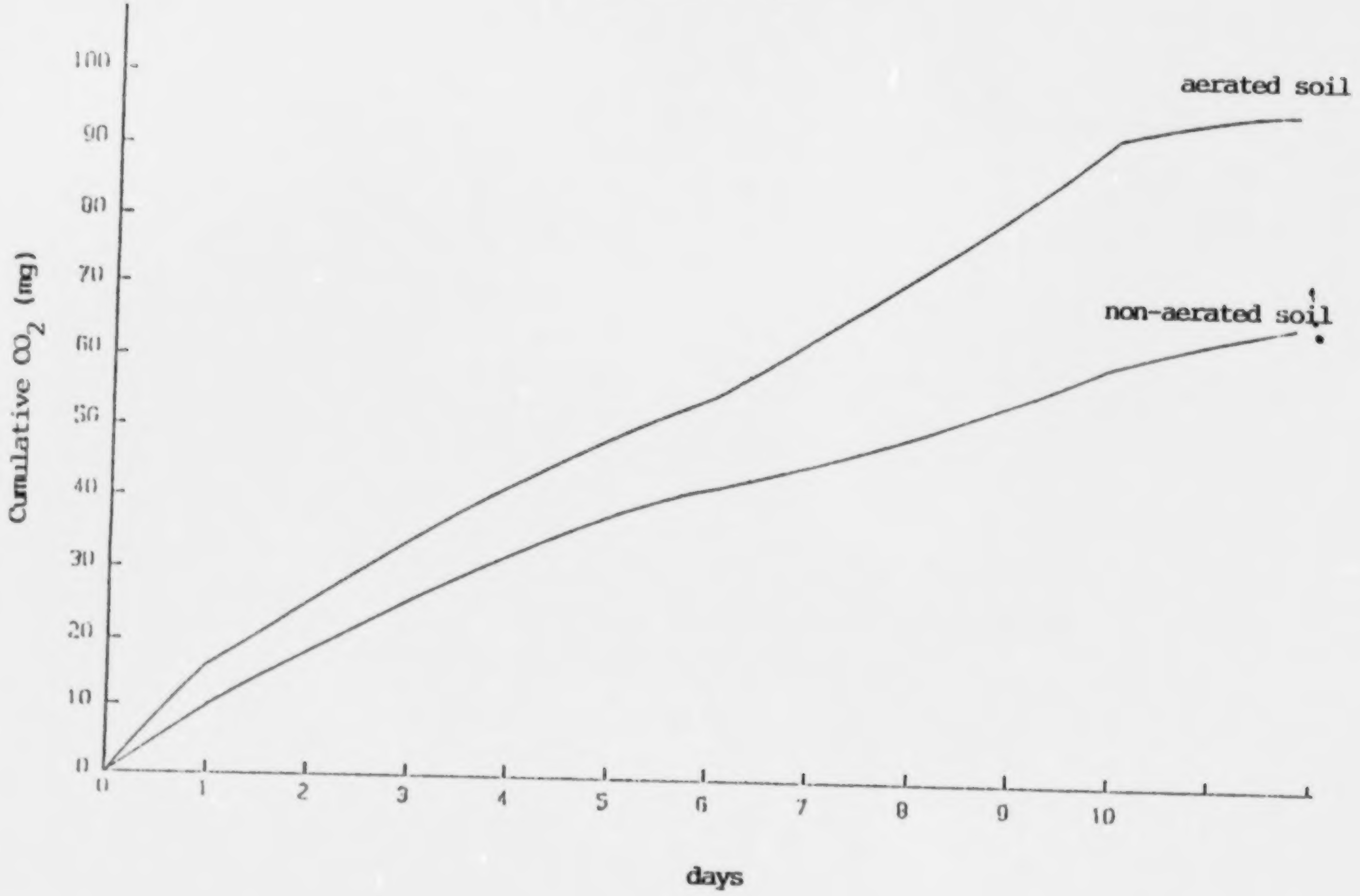


Figure 4 BIODEGRADABILITY ASSAYS CO_2
EVOLUTION CURVES BY INFRA RED DETECTION

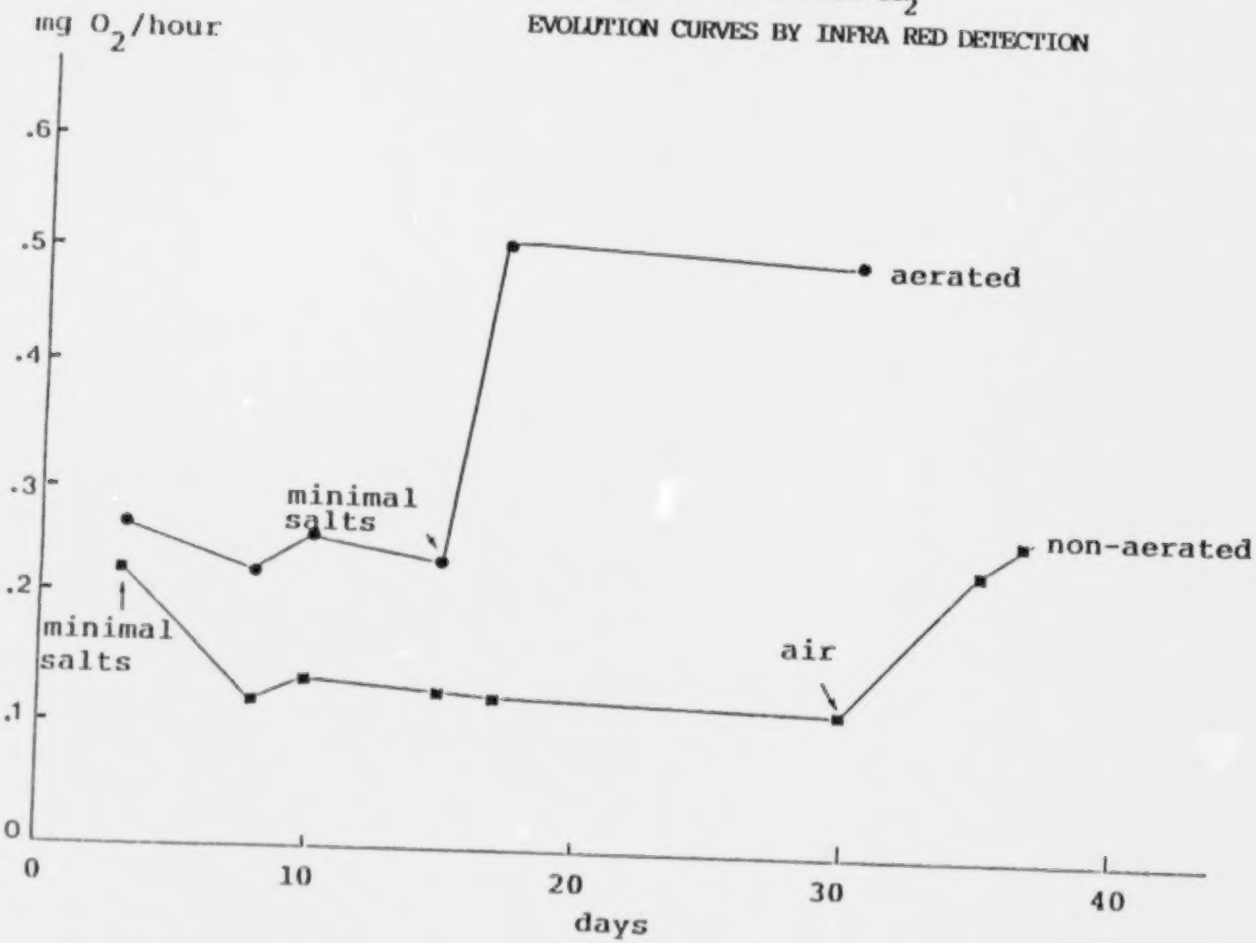


Figure 5 ADAPTABILITY STUDIES
CO_2 EVOLUTION CURVES
BY INFRA RED DETECTION

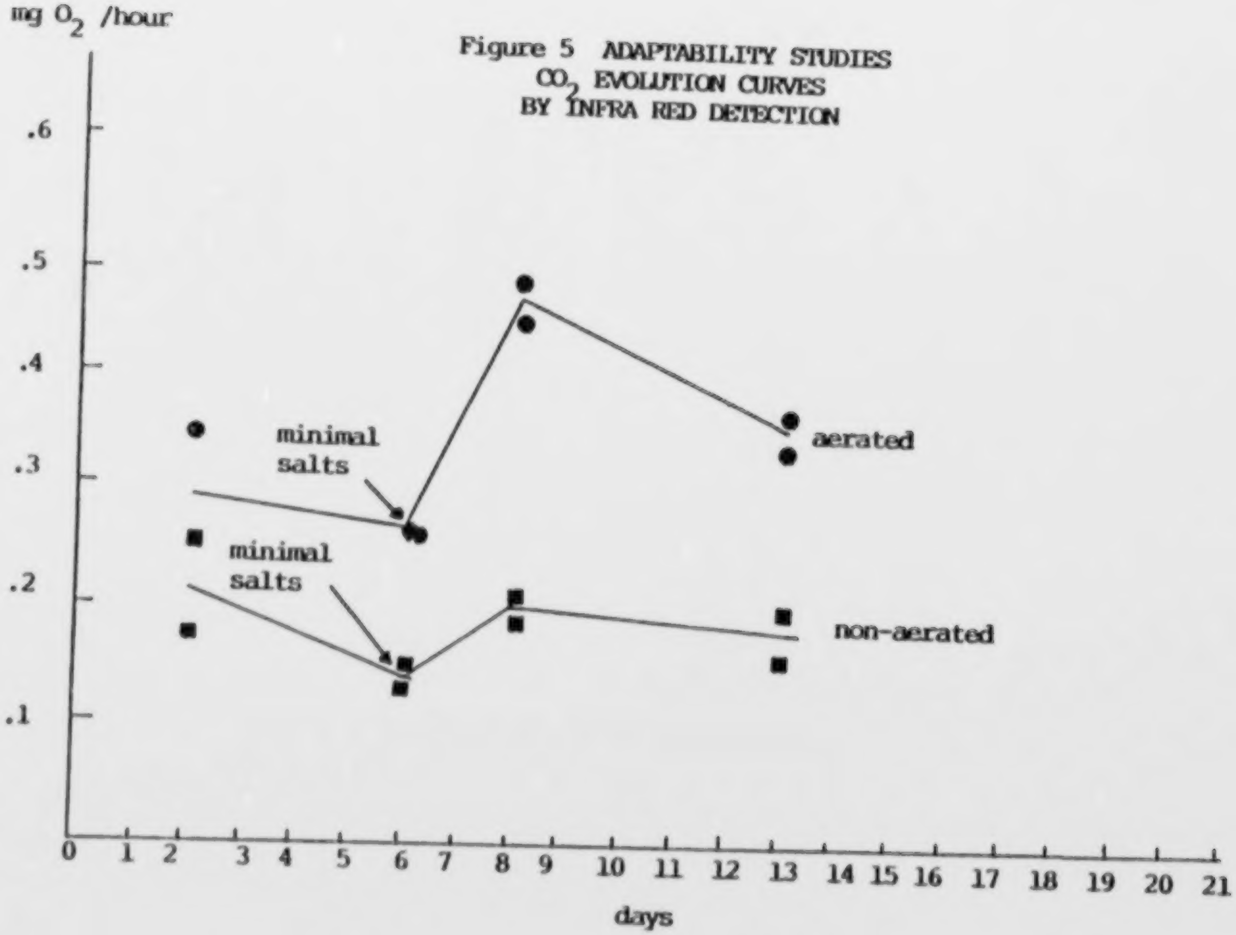


Figure 6 ADAPTABILITY ASSAY CHROMATOGRAMS

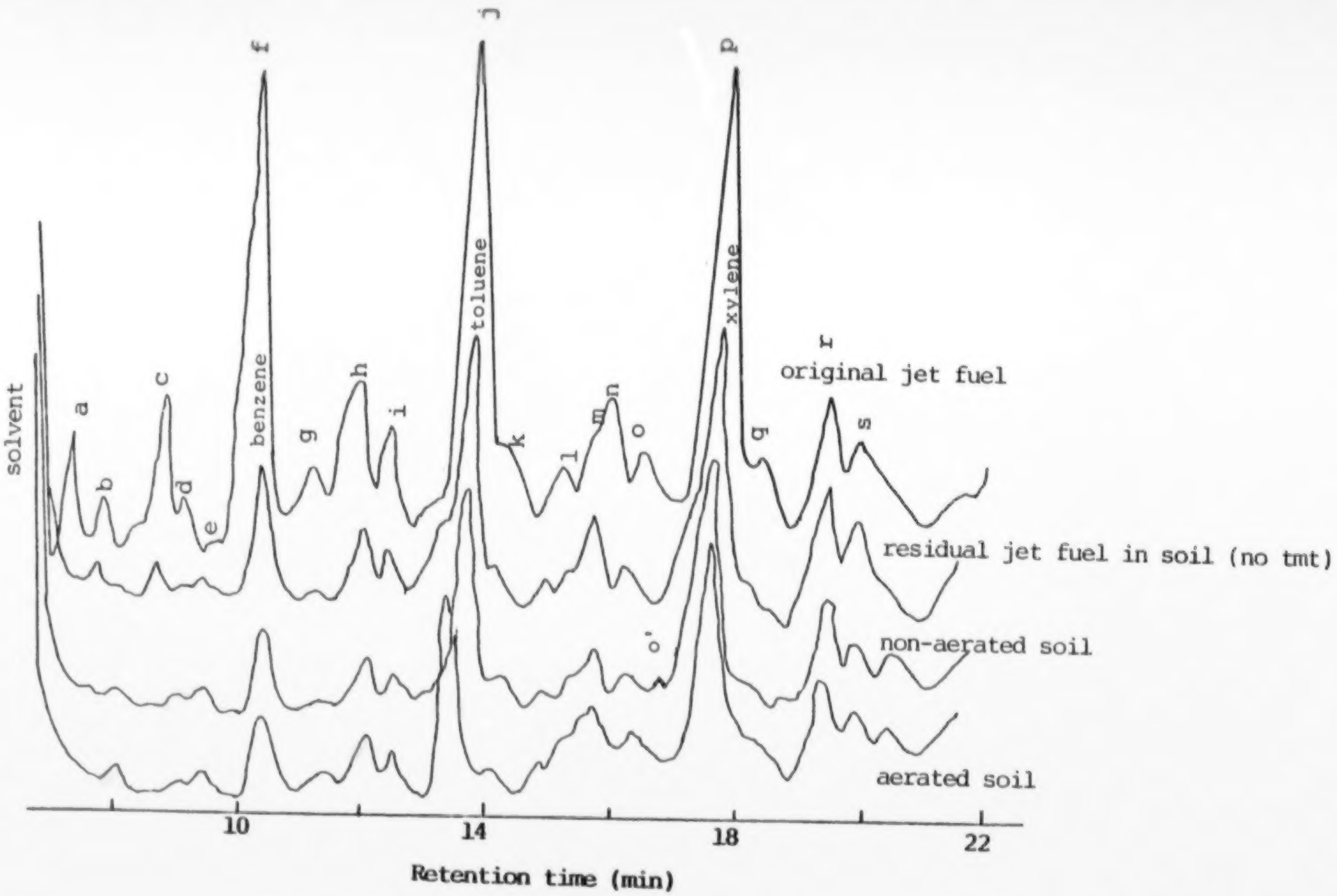


Figure 7 BIODEGRADABILITY ASSAY CHROMATOGRAMS

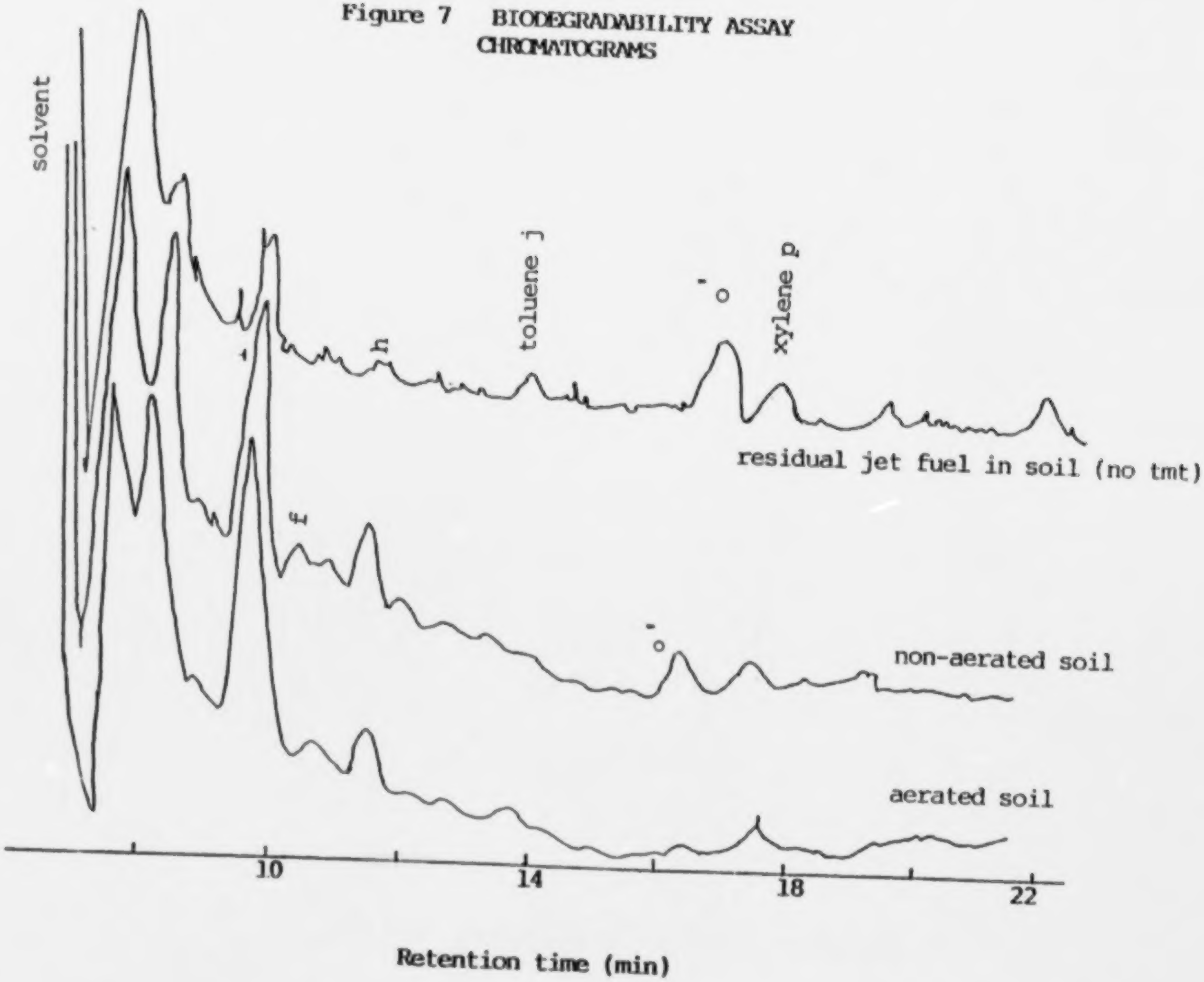


Figure 8 BIODEGRADABILITY ASSAY IR SPECTRA

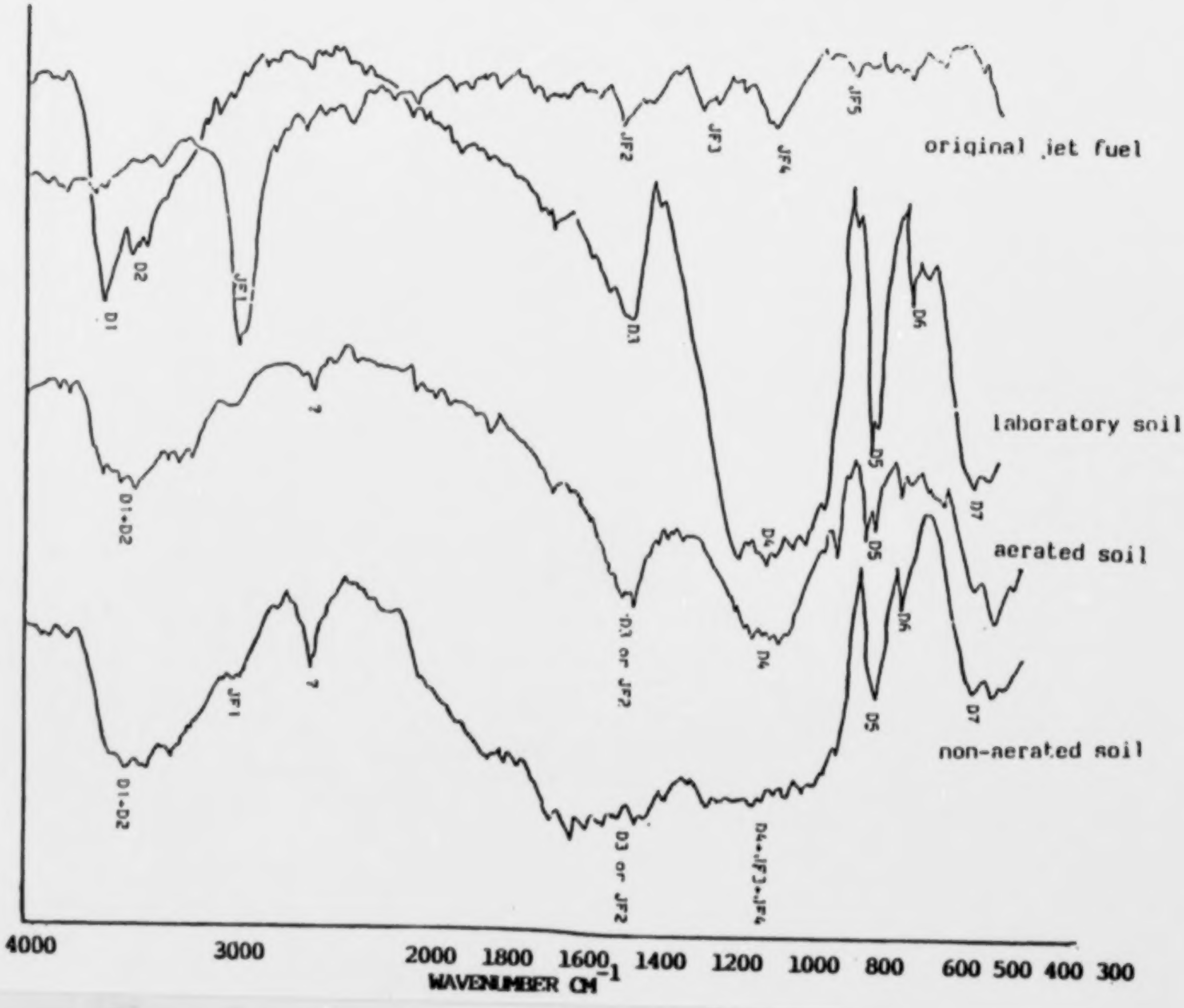
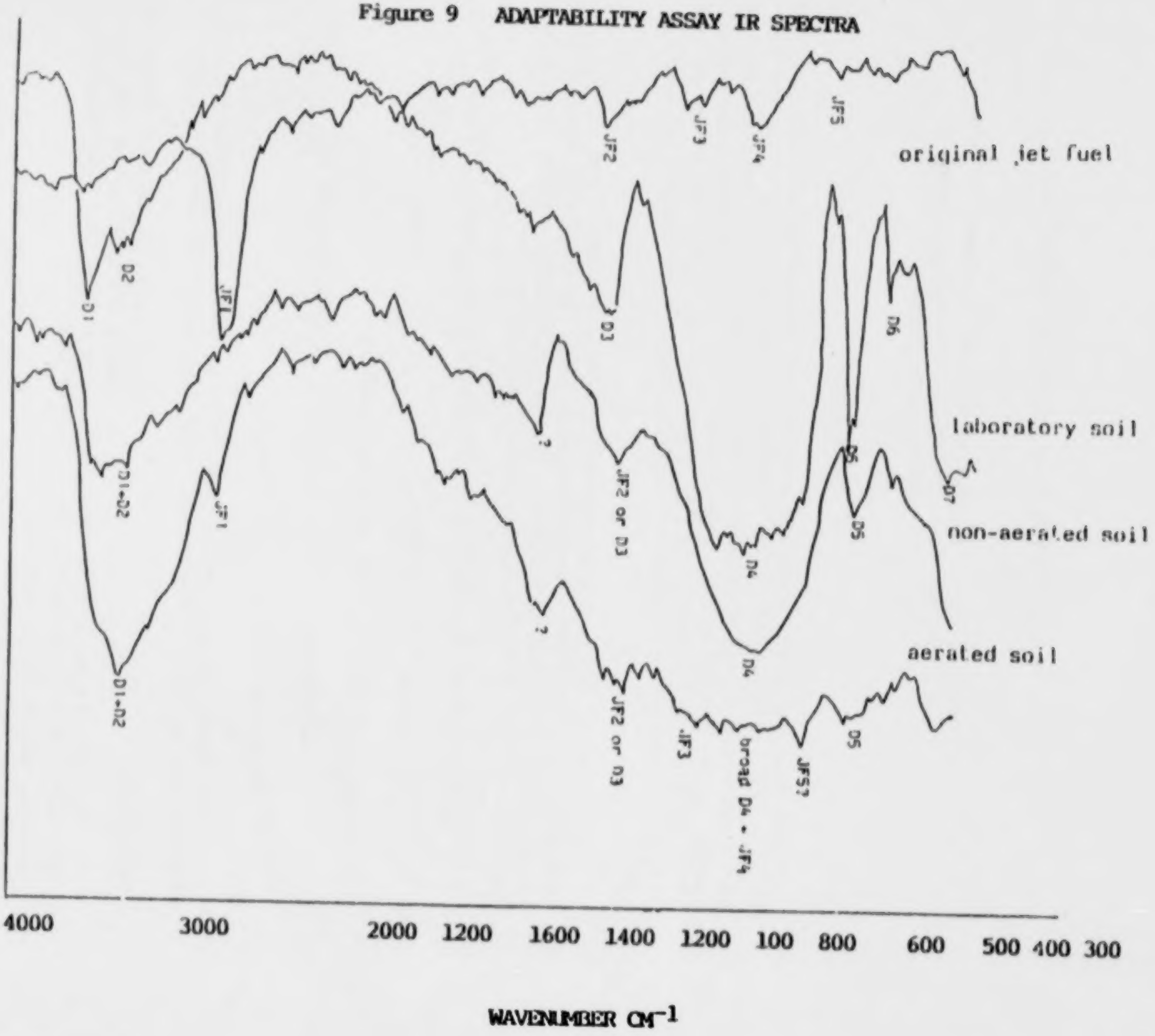


Figure 9 ADAPTABILITY ASSAY IR SPECTRA



BIOLOGICAL TREATMENT OF HAZARDOUS AQUEOUS WASTES

Edward J. Opatken, Hinton K. Howard, James J. Bond
United States Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Studies have been conducted with a rotating biological contactor (RBC) to evaluate the treatability of leachates from the Stringfellow and New Lyme hazardous waste sites located in Riverside County, California and Ashtabula County, Ohio, respectively. The leachates were transported from the waste sites to Cincinnati, where a pilot sized RBC was installed at the United States Environmental Protection Agency's Testing and Evaluation (T&E) Facility.

A series of batches were run with primary effluent from the City of Cincinnati's Mill Creek Sewage Treatment Facility (MCTF) to develop a biomass on the disks and to obtain kinetic removal rate data. These runs were then followed with experiments utilizing leachate that:

- ° Operated at various ratios of leachate to primary effluent
- ° Operated at 100% leachate
- ° Determined the final effluent quality
- ° Determined the fate of specific organic compounds
- ° Determined the rate of removal

This paper reports on the results from these experiments and the effectiveness of an RBC to adequately treat leachates from Superfund sites.

Background

The need to destroy or convert toxic organic chemicals to harmless materials is gaining acceptance. Land disposal is no longer regarded as an ultimate solution for disposing of organic waste because of the potential for leachate formation or groundwater contamination. Leachate releases have taken place from uncontrolled waste disposal sites and provisions are needed to remedy these situations.

Biodegradation of the organics present in leachate may provide an acceptable and cost effective process for treating leachates. For these reasons a study was initiated at the U. S. Environmental Protection

Agency Testing and Evaluation Facility in Cincinnati, Ohio to evaluate a rotating biological contactor[6] to reduce the level of organics in leachates.

Leachate Sources

The initial evaluations were conducted with leachates from Stringfellow, CA, and New Lyme, OH.

Stringfellow is a Superfund site[1] that is located in Glen Avon, California near Riverside, California. The leachate is generated at an approximate rate of 96 m^3/d (25000 gal/d) and contains high concentrations of metals and organics. A leachate treatment facility (1) at the site includes lime treatment for metals removal, followed by clarification, sand filtration, and granular carbon treatment for organics reduction. The effluent from the carbon beds is trucked 19 km (12 mi) to an Orange County interceptor sewer for disposal into the municipal sewer system.

New Lyme is a Superfund site located in Ashtabula County, Ohio (2,3). The landfill received household, industrial, commercial and institutional wastes between 1969 and 1978. Groundwater moves upward through the bedrock into the landfill and under artesian conditions percolates through the landfill and flows out through seeps into the surrounding wet lands.

Project Description

A pilot sized RBC for evaluating the biochemical treatability of Superfund sites' leachates was installed at the EPA Testing and Evaluation Facility located at the Mill Creek Treatment Facility in Cincinnati. The pilot sized RBC contains 1000 m^2 (11000 sq ft) of surface area which is approximately 10% of a full scale RBC(4). The diameter of the pilot unit is 3.6 m (12 ft), which is identical to a full scale RBC. The length is less than 1 m (3.3 ft), whereas a full scale RBC is 7.6 m (25 ft). The MCTF's primary effluent (PE) was used to develop a biological population on the RBC disks and to obtain basic kinetic data on the removal rate of dissolved organic chemicals(5). The ideal conditions would have involved using leachate from the sites to develop an indigenous biomass. However, the logistics favored the treatment plant's PE because of the distance between Cincinnati and the hazadous waste sites. There were other factors which favored conducting the experiments in Cincinnati such as the auxilliary support available for installation, chemical analyses, 24 hour monitoring, and the availability of specialists on biochemical treatment for consultation. The leachates were trucked from the Superfund sites to Cincinnati for experimentation and pumped to a storage tank. The Strinfellow leachate was lime treated at the California site for metals reduction so that the experiments could concentrate on soluble organics removal with the RBC facility. The New Lyme leachate did not require treatment to reduce the level of metals.

The pilot RBC was designed to operate in a batch mode for the following reasons:

- Eliminate flow controls
- Minimize spillages
- Minimize accidental releases into the T&E sewer systems
- Improve mass balance analyses
- Obtain reaction kinetics data
- Control final disposal
- Scale-up for site operation

Objective

The prime objective of this project was to determine whether leachates can be economically converted into innocuous wastes by biochemical treatment with a rotating biological contactor.

Methodology

The RBC was initially operated with primary effluent supplied from the Mill Creek Treatment Facility to develop an adequate biomass on the RBC disks in preparation for leachate treatment.

The first experimental batches for each site were made with increasing ratios of leachate/RBC-treated primary effluent to allow a gradual acclimation period of the biomass to the leachate. Following these batches the runs were made with 100% leachate. A flow schematic of the RBC pilot plant is shown in the attached Figure 1. The operation consisted of transferring the leachate from the storage tank to the mix tank where the volume was determined. It was then pumped to the RBC and operated at a speed of 1.5 rpm. The experiment was considered complete when the dissolved organic carbon (DOC) reached a constant level. For the Stringfellow leachate, the RBC contents were then returned to the mix tank for additional treatment with activated powdered carbon (APC) followed by clarification with ferric chloride to achieve the effluent standards required for disposal to the MCTF. For New Lyme leachate the effluent from the RBC underwent normal clarification before disposal into the sewer system leading to the MCTF.

The effluent limitations set by the MCTF were:

- Total organic halides (TOX) ≤ 5 mg/L
- Vapor space organics(6) (VSO) ≤ 300 ppm
- $6 < pH < 10$

Internal limits were also set on gross organics that were in essence equivalent to a relatively high strength raw wastewater. These limits were:

- Soluble biochemical oxygen demand, SBOD ≤ 100 mg/L
- Dissolved organic carbon, DOC, ≤ 100 mg/L
- Soluble chemical oxygen demand, SCOD, ≤ 300 mg/L

During the experiment the following operating parameters were monitored:

- Volume of leachate fed to the RBC
- Temperature, every 2 hours
- Speed of rotation, every 6 hrs.
- Visual comments on thickness and color of biomass, every 2 hours
- Dissolved oxygen, every 2 hrs.
- pH, every 2 hours
- SBOD, DOC, SCOD.

Kinetic Parameters

During both the biomass buildup and the leachate experiments, samples were obtained from the RBC tank at specified time intervals to obtain a kinetic curve showing the disappearance of the soluble gross organics with time. The gross organics monitored included SBOD, DOC, and SCOD. During each experiment the DOC samples were analyzed immediately to obtain instant information on the progress of the reaction.

In addition to the gross organics the raw leachate and the treated effluent were analyzed for:

- Suspended solids, (SS)
- Volatile suspended solids, (VSS)
- Nitrogen series, including Kjeldahl, ammonia, nitrite, and nitrates
- Phosphorus, (P)

Specific organic analyses were also obtained for the following chemicals on Stringfellow leachate:

- Para-chlorobenzene sulfonic acid (PCBSA)
- 1, 2 dichlorobenzene
- O-xylene
- Chloroform
- Ethylbenzene
- 2-hexanone
- Tetrachloroethylene

Specific organic analyses obtained on New Lyme leachate and effluent included:

- Priority pollutants
  - volatile compounds
  - base-neutral compounds
  - metals
  - acid compound
  - pesticide and PCB compounds

Results and Discussion

The rate of soluble organic removal was determined for the Mill Creek primary effluent by following the disappearance of SBOD, SCOD and DOC with time. A typical curve for the disappearance of soluble organics using PE was used as a base (see Figure 2) for comparison with data obtained on PE following experiments with leachate, to determine if the biomass had undergone deterioration by the leachate. See Figure 3 and compare this result with Figure 2 as an example of the drop in removal rate following an extended experimental batch with leachate.

Biomass Acclimation

Since the biomass established on the RBC disks was developed with primary effluent, acclimation runs were made using the leachates diluted with primary effluent to avoid shock loading the biomass with 100% leachate. The Stringfellow leachate was three to four times stronger in organic concentrations than the PE and contained a significant quantity of p-chlorobenzene sulfonic acid, (PCBSA) a compound that is foreign to the biomass. The New Lyme leachate was 20 times stronger in organic concentration than PE.

The acclimation period consisted of experimental runs using progressively stronger concentrations of leachate as shown below.

The ratio of leachate to PE

For Stringfellow

- Batch # 1: Leachate/treated PE = 1/2
- Batch # 2: Leachate/treated batch # 1 = 1/1
- Batch # 3: Leachate/treated batch # 2 = 3/1

For New Lyme

- Batch # 01: Leachate/PE = 1/2
- Batch # 02: Leachate/PE = 2/1

When Stringfellow leachate was combined with treated PE in batch # 1 there was a six day lag period before the DOC began to disappear. (See Figure 4.) After the incubation period the reaction required approximately 2 days to obtain a drop of approximately 60% in the DOC. The residual DOC, approximately 50 mg/L, remained unchanged during an additional 6 days of treatment.

In batch # 2 the reaction for the disappearance of DOC began after the first day and was essentially complete after three days. The percent removal of DOC was approximately 50% and the residual DOC was approximately 90 mg/L. The result for batch # 3 was similar to batch # 2. That is, the reduction in DOC was essentially complete after three days. The DOC removal was approximately 55% and the batch had a final DOC of 120 mg/L.

Batch # 3 was continued for an additional 27 days to determine if an extended time period would result in a further reduction in DOC The additional time had no effect on DOC. However, this added reaction time resulted in the sloughing off of the biomass and was the cause of the drop in reaction time when PE was tested to determine the reaction rate, as shown in Figure 3.

When New Lyme (NL) leachate was mixed with PE at a ratio of 1 part NL/ 2 parts PE, the reaction started immediately and the organics were converted to innocuous products in less than 20 hours. (See figure 5.)

The removal was 97% for the gross organics and the quality of effluent was far superior to many secondary effluents from wastewater treatment plants when compared on the basis of final gross organic concentrations.

Batch # 02 had radically different results. The NL/PE ratio was increased to 2/1 and there was an ineffective rate of removal. The results indicate:

- ° The removal progressed at a very slow rate, as depicted in Figure 6. Instead of 20 hours of reaction time, it took 300 hours to complete the reaction.
- ° The biomass was stripped from the discs. This was evident by visual observation of the suspended solids. To confirm this, a run was made using PE. Figure 7 shows that the disappearance of the organics was at a significantly lower rate of removal in contrast to the satisfactory results obtained earlier with PE. Since the speed of rotation for all runs was made at 1.5 rpm it was assumed that the oxygen transfer rates were unaffected (7). The substrate concentration using PE was similar, so the only factor remaining that could cause the fall-off in organic disappearance was the biomass level. This supported the visual evidence of biomass stripping and the increased concentration of the suspended solids in the RBC tank contents.

Operation with 100% Stringfellow Leachate*

Following the Stringfellow acclimation runs, a series of experiments were made using 100% Stringfellow leachate. The results were similar to those obtained during the acclimation runs 2 and 3. (See Figure 8.)

- ° Approximately four days were required to reduce the DOC from 300 to 100 mg/L. This closely approximates the results obtained with the leachate and PE mixture and is in contrast to only 2 hours that is needed to obtain a large DOC reduction using PE.

---

*As of this writing no runs have been made with 100% New Lyme leachate.

- The removal rate was significantly below the rate obtained with PE. Previous work on RBC's showed a SBOD removal rate of 440 $\text{mg/h}\cdot\text{m}^2$ (4) (41 $\text{mg/h}\cdot\text{ft}^2$) with municipal wastewater; whereas the Stringfellow leachate gave 19 $\text{mg/h}\cdot\text{m}^2$. (1.7 $\text{mg/h}\cdot\text{ft}^2$).
- The RBC operation required pH adjustment. As the DOC dropped during the reaction phase the pH would fall and require periodic additions of sodium hydroxide to maintain a pH greater than six.
- It was necessary to add sodium phosphate to the leachate to provide adequate levels of P to maintain a satisfactory supply of nutrients (8).
- Characterization of the leachate indicated that nitrogen was readily available as nitrate and therefore no adjustment was needed in regard to nitrogen.
- The major identified organic constituent, p-chlorobenzene sulfonic acid, was readily removed during the RBC treatment.
- The residual DOC was not identified by a GS-MS scan, because of the nature of the compound/compounds.
- The leachate final concentrations were

  110 mg/L of DOC
  1 mg/L of SBOD
  370 mg/L of SCOD

These results showed almost 100% removal of biodegradable organics as defined by SBOD. They also showed that a significant fraction of refractory organics remained after the treatment. Only 63% of the DOC was removed and only 54% of the SCOD was removed.

In order to meet the limits specified for disposal into the Mill Creek Treatment Facility, it was necessary to treat the leachate with activated powdered carbon to remove additional refractory organics. The RBC contents were transferred to a mix tank where 12 to 15 grams of activated carbon per gram of DOC were added. Separation of the carbon from the leachate was achieved by flocculation with ferric chloride during clarification. The previously specified limits were met:

- TOX <5 mg/L
- VSO $\underline{<}$ 300 ppm
- $6<\text{pH}\overline{<}10$
- DOC <100 mg/L
- SCOD <300 mg/L
- SBOD <100 mg/L

Conclusions

Although the organics in Stringfellow leachate were not totally biodegraded, a significant reduction was achieved. The DOC was reduced by two thirds, the SCOD was reduced by one-half, and the SBOD was completely eliminated.

The refractory fraction following RBC treatment was not identified by a GC-MS scan and the organics constituting 1/3 of the total organics at Stringfellow remains unidentified.

Leachates from different hazardous waste sites have unique compositions, and it can be expected that each will react differently to RBC treatment. The leachate characterization is important to obtain an indication of its biodegradability. The experience with Stringfellow showed the pH dropped as the reaction progressed, yet at New Lyme the pH rose, so the behavior is not predictable. The DO levels were satisfactory, usually above 5 mg/L, with both leachates indicating that biomass levels were probably controlling the reaction kinetics. The reaction rates were significantly different when comparing the two leachates. At Stringfellow the reaction rate required approximately 4 days to convert the SBOD, whereas New Lyme required only 20 hours and yet the initial SBOD concentrations were three-fold higher than Stringfellow. With New Lyme leachate, increasing the ratio of NL/PE from 1/2 to 2/1, significantly affected the reaction rate, possibly indicating either an inhibiting organic or insufficient nutrients.

It is clear that the RBC offers a high degree of promise for cost effectively treating leachates from hazardous waste sites; however more research is needed to confirm these findings and to better define the effectiveness of the RBC treatment of leachates.

References

1. Internal Memo "Stringfellow Pretreatment Plant Operation and Maintenance Costs," Camp, Dresser & McKee, September 1986.

2. Draft Report of "Treatability Testing and Field Investigation Report New Lyme Landfill," U. S. Army Corps of Engineers, Omaha District, January, 1987.

3. Final Remedial Investigation New Lyme Landfill Site, Ashtabula County, Ohio, CH_2M-Hill, February 6, 1985.

4. Brenner, R. C., Heidman, J. A., Opatken, E. J., Petrasek, A. C., "Design Information on Rotating Biological Contactors," EPA-600/2-84-106, June, 1984.

5. Opatken, E. J., "An Alternative RBC Design - Second Order Kinetics," Environmental Progress, Vol. 5, No. 1, February, 1986.

6. "Vapor Space Organics," In-house method developed by the Metropolitan Sewer District of Greater Cincinnati, Industrial Waste Section, Cincinnati, Ohio.

7. Antonie, R. L., Fixed Biological Surfaces - Wastewater Treatment, CRC Press, 1976.

8. Record of Decision, "Remedial Alternative Selection," Stringfellow Acid Pits, Glen Avon, California, U.S. EPA, Region IX, San Francisco, CA.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

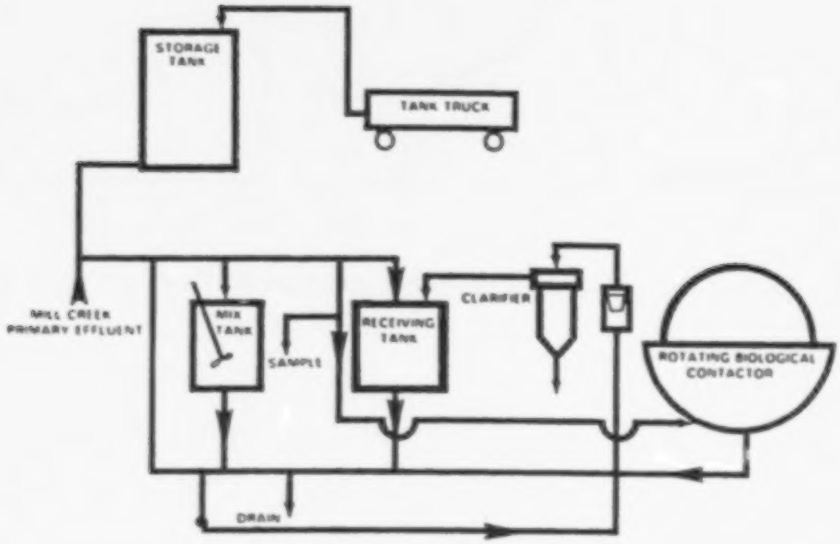

STORAGE TANK
TANK TRUCK
MILL CREEK PRIMARY EFFLUENT
MIX TANK
SAMPLE
RECEIVING TANK
CLARIFIER
ROTATING BIOLOGICAL CONTACTOR
DRAIN

Figure 1 Stringfellow—RBC Flow Schematic

Primary effluent Run #2 3/5/86

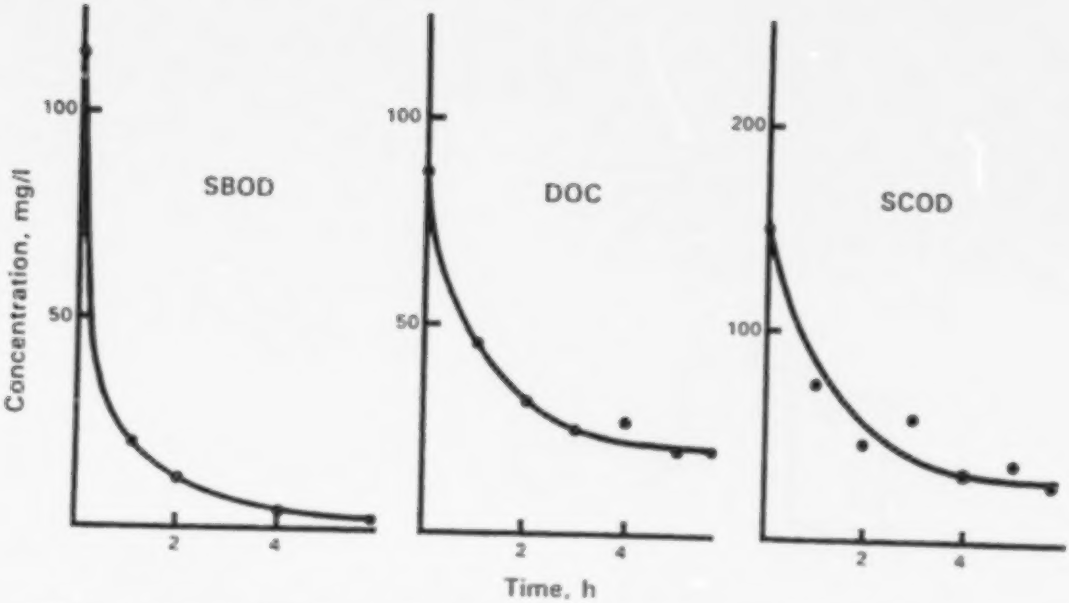


Figure 2 Standard Rate for the Biodegradation of Primary Effluent

Primary effluent after Batch 3 6/4/86

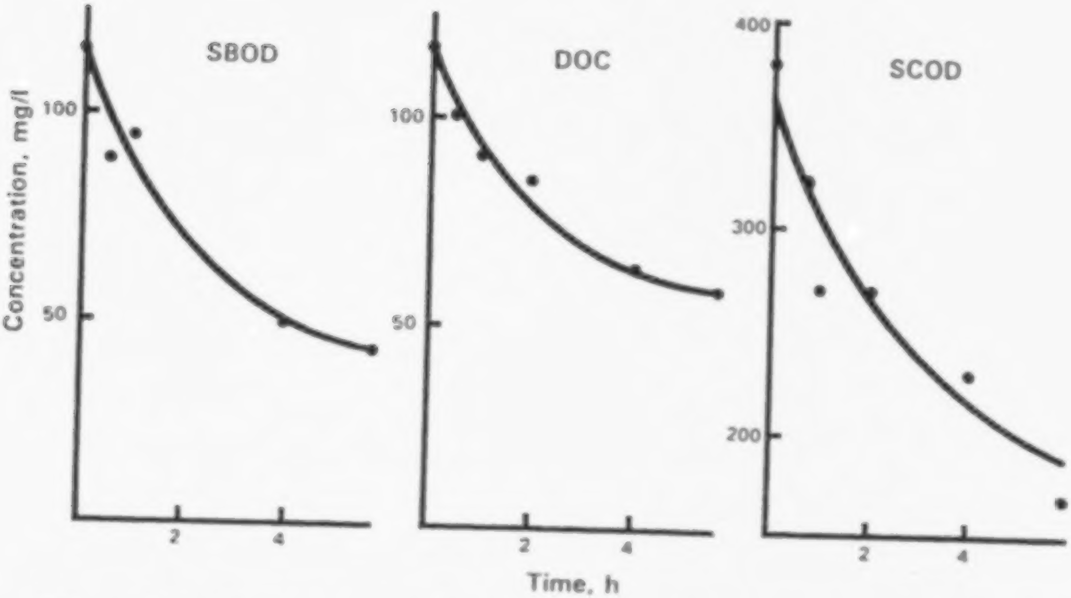


Figure 3 Disappearance of Organics After Stringfellow Run-03

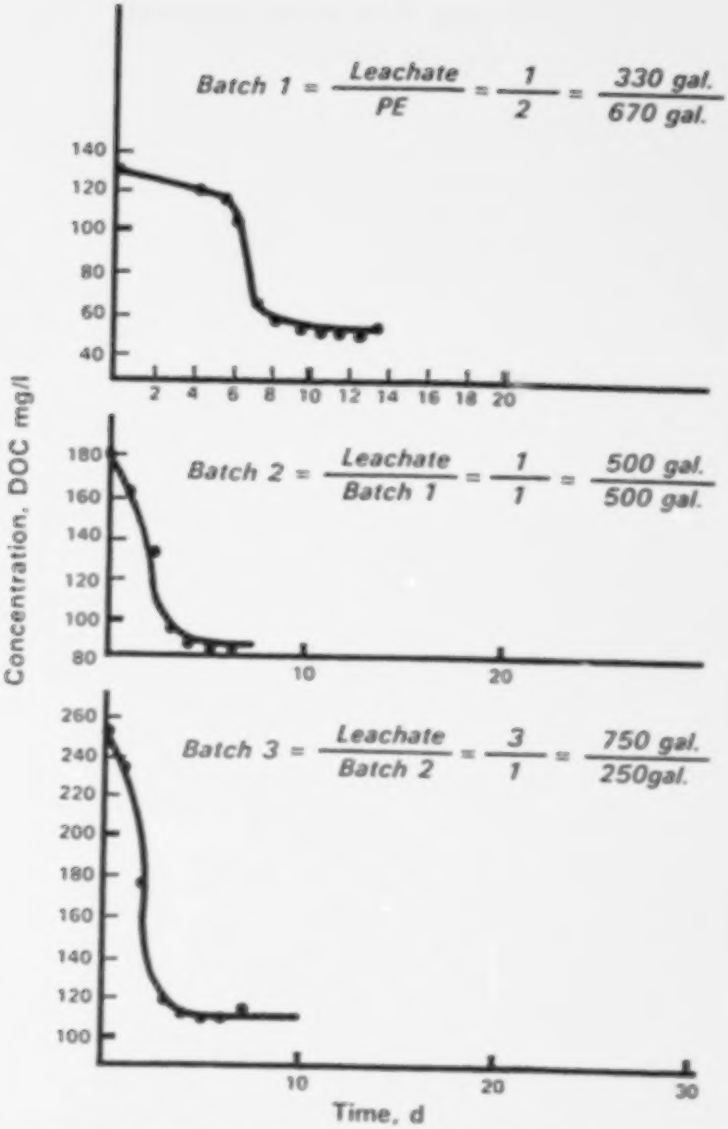


Figure 4 Disappearance of DOC With Time Using Various Ratios of Leachate to Treated Effluent

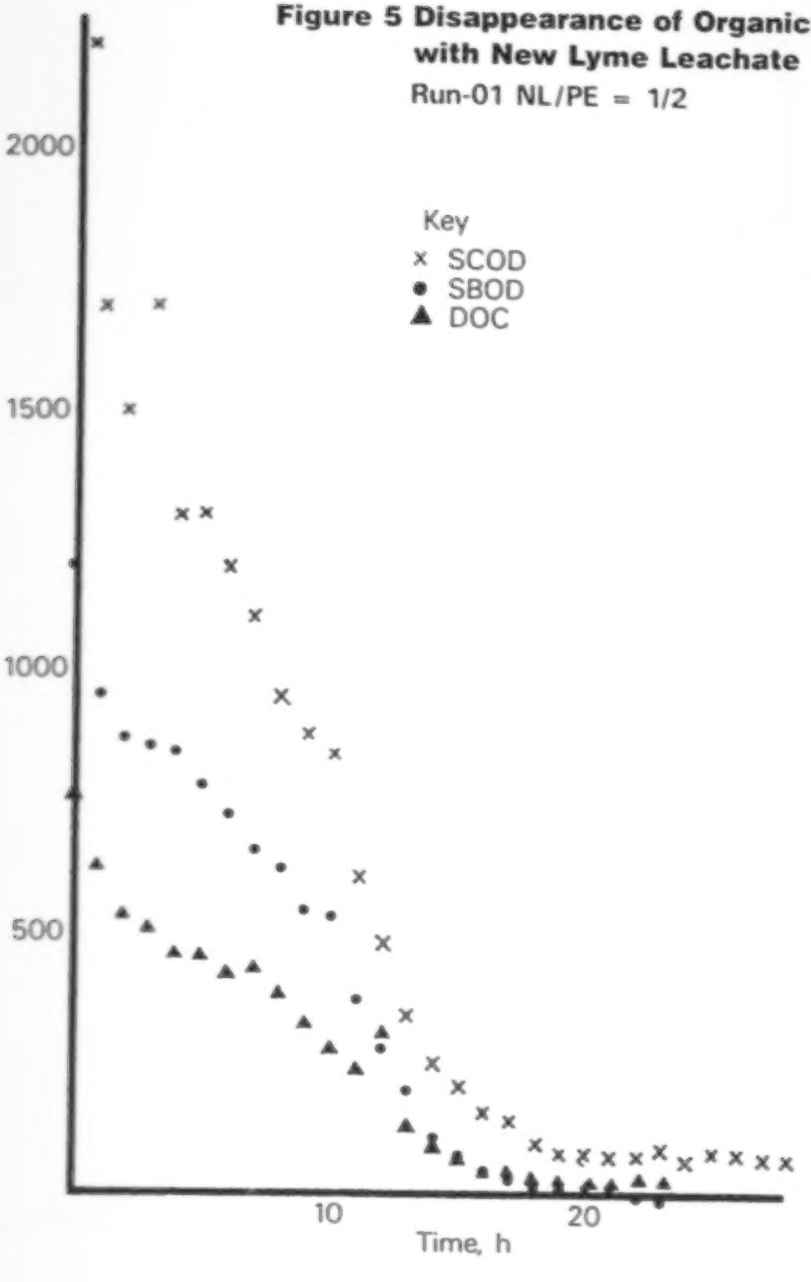


Figure 5 Disappearance of Organics with New Lyme Leachate

Run-01 NL/PE = 1/2

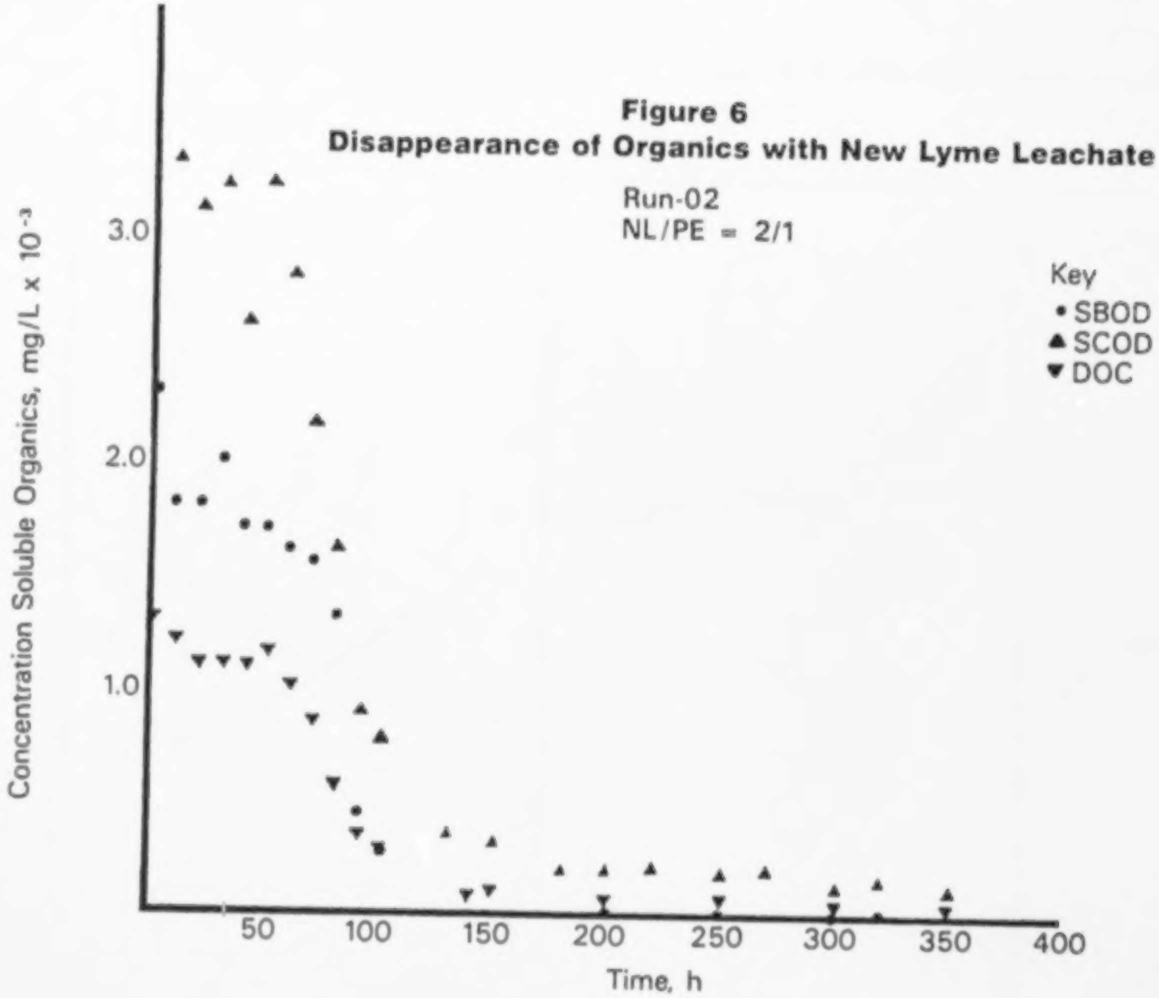


Figure 6
Disappearance of Organics with New Lyme Leachate

Run-02
NL/PE = 2/1

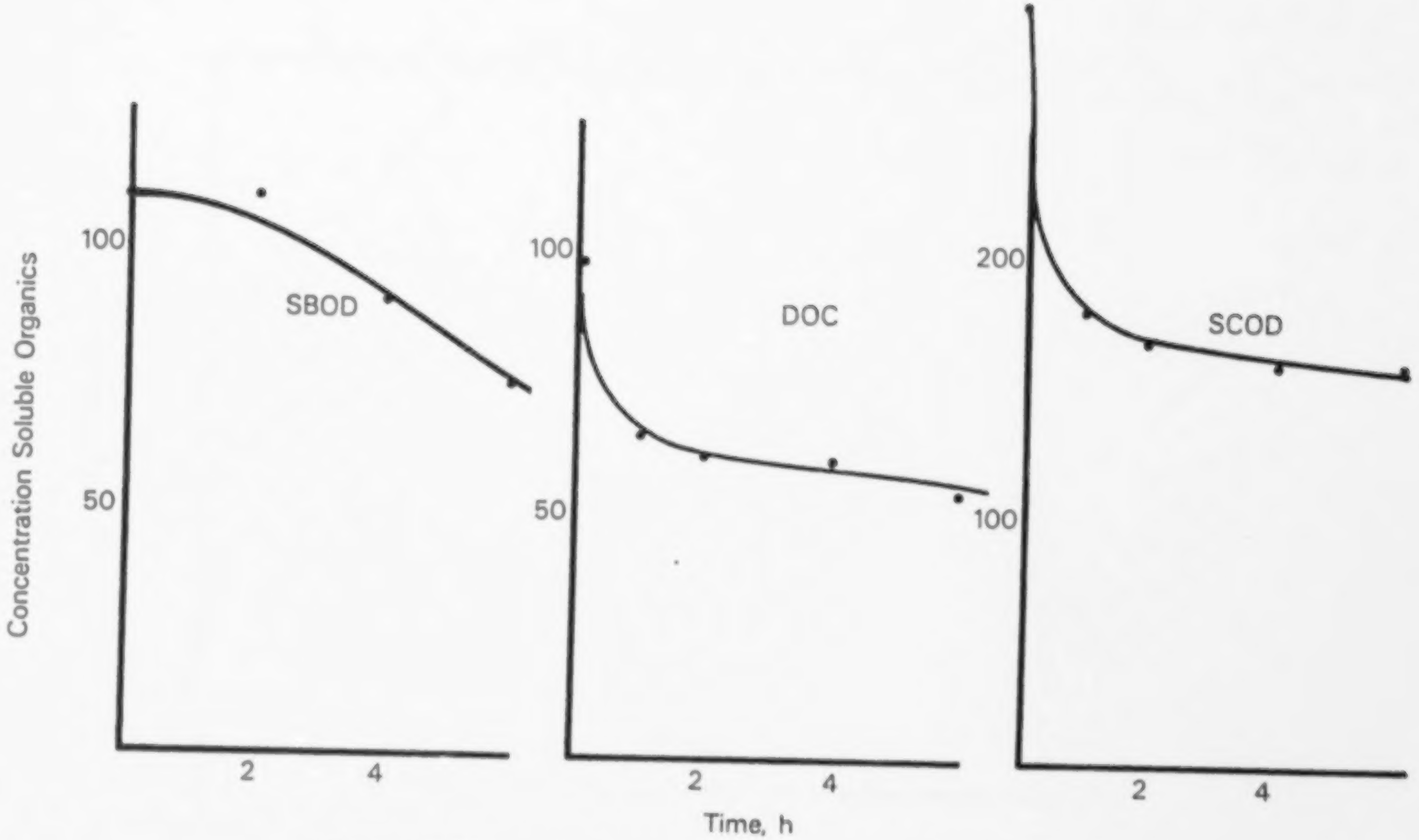


Figure 7 Disappearance of PE Organics After New Lyme Run-02

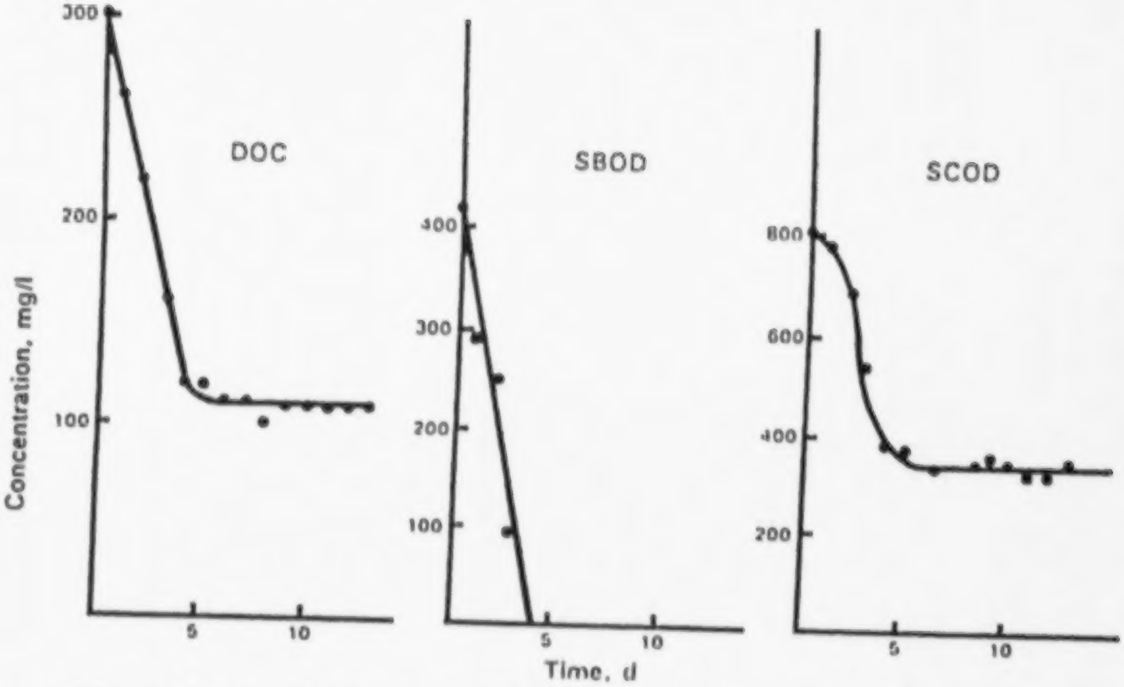


Figure 8 Disappearance of Organics for 100% Stringfellow Leachate

Feasibility Study on Disposal of Oily Sludge in Kuwait

Amin S. ElNawawy, Fikry H. Ghobrial and Abdelghani A. Elimam

Kuwait Institute for Scientific Research
P. O. Box 24885
13109-Safat-Kuwait

ABSTRACT

The results presented in this paper are part of the solid waste management program developed for the Shuaiba Industrial Area (SIA) which accommodates several industries in Kuwait. Based on the information obtained through questionnaires and field survey, the quantity of oily sludge is estimated at about 65,000 t/yr. This sludge is at present dumped in special pits in desert areas. The water content of the oily sludge ranges between 40-80%.

Several technologies for handling the oily sludge were discussed but only two, incineration and landfarming, were considered as suitable candidate technologies for further technical and economical analysis. Technical assessment showed that incineration can be implemented immediately because it is readily established technology. Two rotary kiln type incinerators, each of capacity of 5.5 t of oily waste per hour are proposed. Remaining ashes are assumed to be landfilled in a lined cell of the landfill facility recommended for the disposal of general solid wastes. The technical assessment showed also that landfarming is an attractive method but should be investigated further under local conditions. It was suggested that application of oil on land should not exceed 15 kg per m^2 and initial trial should start with 5-10 kg per m^2. Cost analysis indicated that landfarming presents the least cost alternative to handle oily semisolid wastes. Moreover it presents an excellent opportunity to increase the cultivable land and contribute to the agricultural development in Kuwait.

INTRODUCTION

A comprehensive study of solid and semisolid waste problem in SIA was carried out during the period of 1983-85 with the aim of suggesting an integrated waste management program for the area (ElNawawy et al., 1986a, b). During this study, the oily sludges proved to be the major semisolid wastes in the area. About 65,000 t of oily sludge are generated annually. At present, this waste is dumped in lagoons without any environmental control measures. The study considered alternative methods for proper handling of oily sludge, i.e., incineration and landfarming. The technical, economical and environmental aspects of these two candidate technologies are discussed in the present paper.

PURPOSE

The main objective of this paper is to present Kuwait experience in handling and/or disposal of oily sludge based on the findings and recommendations of the feasibility study on alternative candidate technologies.

APPROACH

Data Collection

Data were collected for different types of solid and semisolid wastes generated in the industrial area through questionnaires followed by visit to industries. This included their types, quantities, character, and location of sources as well as present treatment and/or disposal method. Oily sludge was identified mainly in Kuwait Oil Company (KOC) refinery, and Kuwait National Petroleum Company (KNPC) refinery at more than one location.

Assessment of Alternative Technologies

Technical and economical assessment of candidate technologies (incineration and landfarming) were carried out. The factors influencing process performance, number of needed units or area requirements, environmental aspects, operation and maintenance requirements, and needed further investigations were pointed out. Cost analysis took into account the cost of transport as well as cost of technology proposed for the treatment and/or disposal of oily sludge

PROBLEMS ENCOUNTERED

Due to lack of compulsory regulations, and underestimation of the pollution load of generated waste, there are lack of both consistent records and accurate information on the characters and quantity of generated wastes.

RESULTS

Oily Sludge

As shown in Table 1, oily sludges originate from the crude oil itself, oil processing, and waste oil products. They are generated during maintenance of storage tanks and as precipitates in the API separator. Oily wastes are dumped by tank trucks to pits in desert area; leaded sludge (300 ppm lead) is incinerated in a specially controlled cement pit.

The oily sludge has a water content that ranges between 40-80%. Analysis of the sludge from bottom tanks are shown in Table 2.

Technical Assessment of Alternative Technologies

Recycling or recovery options are apparently the most attractive options for the bulk of the oily wastes produced in the SIA. The most profitable recovery option would be as supplementary fuel for a large fuel consumer. This would necessitate dewatering of these wastes as far as reasonably practicable to enhance the heat values of the wastes. Based on the information obtained from the survey, such a consumer does not exist in the vicinity of the industrial area. Another option for reuse is to mix the sludge with lime dust generated from the electrostatic precipitator of the lime products industry in SIA (15,000 t/y) to form a liner. However, implementation of this option would necessitate further study to select the appropriate conditions for optimal mixing, test the properties of such a liner and determine its potential local market demands. Such technology may result in the least cost option, if the product is used for lining landfill pits within the SIA.

Incineration. Incineration technology is well established. It is relatively expensive. Incineration has been used for a wide range of wastes particularly those of organic origin such as oily wastes. In the market, there are many different kinds of incinerators for handling ranges of wastes of different physical forms.

Effective incineration demands a controlled fuel that does not vary too much in quantity, calorific value, or physical form. Since combustion usually occurs in gas phase, burning gases must be held at a high enough temperature, with the right degree of turbulence, for enough time to complete combustion. These factors as well as the size and characteristics of the wastes

Table 1. Sources and Quantities of Oily Sludges

Types and Source of Sludge	Amount (t/yr)
Oily sludges*	15,000
Bitumen sludge*	113
Leaded sludge*	30
API sludge**	300
Maintenance tank sludge	20,000
Tank bottom sludge	11,100
KOC Ahmadi	15,000
KOC Wafra	3,120
Tank bottom sludge*	1,700
TOTAL	66,363

*Kuwait Oil Company Refinery
**Kuwait National Petroleum Company Refinery

Table 2. Analysis of Tank Bottom Sludge

Parameter	Fresh
Moisture (%)	41.9
Density (g/ml)	0.87
Organic matter (%)	52.28
Ash (%)	5.85
Sulfur (%)	1.65
Metals (ug/g)	
Cadmium	BDL
Chromium	95.0
Copper	137.0
Iron	622.0
Nickel	38.0
Lead	8.0
Arsenic	BDL
Heat content	9.5

BDL = below detection limits

govern the design of the appropriate incinerator. For many wastes, a combustion zone for 0.5-1 second is usually adequate, particularly the wastes of SIA do not contain significant quantities of organochlorine compounds. For design purposes, it has been assumed that 60% of the incinerable wastes will be liquid and 40% will be semisolid. Two rotary kiln type incinerators, each of maximum handling capacity of 5.5 t of oily wastes per hour, are proposed to ensure that all of the liquid wastes can be handled by a single kiln during periods of shut-down of one of the kilns during maintenance or emergency. Storage facilities should be provided for semisolids and liquid wastes to cater for fluctuations in the rate of supply as well as periods of shut-down. The remaining wastes after incineration (ash) are assumed to be disposed of in a secure landfill. The incineration plant is assumed to be in operation for 312 days per year on the basis of three shift per day. Most of this time, the two incinerators will be simultaneously in operation each at a rate of 3.5 t of oily sludge per hour. Each incinerator is assumed to be out of service for about 2-4 weeks every three months for maintenance.

All incinerators produce combustion gases that can have significant environmental impact. Incinerating wastes containing significant quantities of elements other than carbon, hydrogen, and oxygen will result in combustion products such as HCl, SO_2, P_2O_5, and NO_2. Combustion gases may also contain volatile inorganic materials such as heavy metals. This, however, is unlikely to be the problem in a well-operated incinerator handling the oily wastes of SIA. However, wastes to be incinerated should be examined with regard to their possible emissions and combustion gases must be treated to comply with relevant rules and regulations for clean air. It is proposed to introduce fuel gas cleaning system and exhaust gas scrubbing system in the incinerators of SIA to ensure compliance.

Landfarming. Landfarming is the other attractive method for the disposal of a fairly wide range of organic wastes, including oily sludge. This method depends mainly on the natural in-situ biological decomposition of hydrocarbons by the vast and varied population and micro-flora in natural soils associated with photodegradation. The method involves the judicious application of wastes in controlled quantities to the land, the application of fertilizer, and regular planting of appropriate crops. Off-site monitoring is usually installed to detect the possible migration of pollutants. This method is widely practiced, particularly in North America, where it is successfully used in a wide range of soil types and climatic conditions. Half of the total volume of oily wastes in the USA are disposed of using this method (Arora et al., 1982, Bonnier et al., 1980).

The motivations and advantages to use this method in Kuwait include:

- the use of proven technology of established effectiveness in other countries.
- improving soil fertility and its water holding capacity (WHC).
- increasing the needed green areas at a comparatively low cost
- the proximity of available land to the source of the wastes
- the arid climatic conditions (long hot summer period).
- the relative process simplicity requiring least maintenance.

Based on sludge characteristics, the types of sludge suitable for landfarming include all homogeneous sludges containing oil, water and solids and these are tank bottoms, desalter bottoms and gravity separation bottoms which constitute the bulk of the oily sludge in SIA (about 53,000 t/yr).

The fate of oily wastes at a landarming site depends on the relative composition of oil in the sludge and the structure of the soil.

The structure of the soil and its humus content are major factors in the process of hydrocarbon decomposition, as they influence oil and water retention, the kind and number of microflora, and the rate of oxygen transfer. For sandy soils, such as the local soil, the total oxygen supplied is estimated at 1.2 kg per m^3 per year. It has been documented that the rate of decomposition is highest in black podsol soil which contains large number of microorganisms, high humus content, and is permeable. Favorable soils for sludge farming include sandy loams and silty loams (Bonnier et al., 1980, Brown et al., 1982.).

It is suggested that application of oil should not exceed 15 kg per m^2 and initial trials should start with 5-10 kg per m^2 (Bonnier et al., 1980).

The applicability of landfarming in Kuwait, however, would have to be considered in depth. The major contaminants of concern in oily sludge that must be considered are the heavy metals. These can have an effect on the microbiological population by biocidal action, on the fertility of the soil for crops and the use of those crops. Other factors that need to be taken into account are the extent of need for fertilizer, climate, microbial population, pH, application rate and method, and waste characteristics (Phung 1978; Hornick et al., 1983).

Environmental issues such as the presence of oily odors during initial spreading, ground water pollution due to leaching and movement of hydrocarbons and/or heavy metals, and health problems associated with the contact with oily sludges are among the concerns which will be considered during further investigation.

Accordingly, a separate study has just started in October 1986 to optimize the biodegradation rates of oily sludges in Kuwaiti soils. Preliminary information indicates that the Kuwaiti soil has pH > 7.5, and its saturation rate with oily sludge was 15% (W/W). The sludge used contained 25% oil. Different ratios of oil (5-15%) with or without inorganic nitrogen and phosphate fertilizers are being investigated under local conditions.

Cost Analysis

Cost for alternative technologies for handling and/or disposal of oily sludge, namely, incineration and landfarming, were based on unit cost information obtained from manufacturers, consulting offices and the local market. Cost analysis was conducted to identify the least cost alternative on the long term.

Incineration Cost. The two incinerators are expected to handle about 53,000 t/yr of oily sludge. The selected air cooling incineration facility is costed using the following cost function:

$C = 81733 + 57983\ P \quad \text{for } P > 3\ t\ h^{-1}$

where

P is the installed capacity of the incineration facility, t/h.

C is the annualized total cost of the incineration facility, KD

The annualized total cost of the incineration facility, based on a life time of 20 years and a discount rate of 8%, is estimated to be KD. 720,000. The annual transportation costs for the wastes to be incinerated are evaluated for two alternative locations of the incineration facility and these were estimated at KD. 47,126 and KD. 47,671 respectively which shows no significant difference.

Landfarming. The proposed landfarming site is at a distance from the SIA (about 60 km) which makes the transportation costs associated with this alternative of significant importance especially not only the oily sludge will be transported to the site but also irrigation water rich in nitrogen as needed. The required quantity of irrigation water will depend on moisture content of sludge as well as on climate. For this reason, the present study considered three scenarios. In the first scenario, no irrigation water would be needed. In the second and third scenarios 1 and 2 m^3 of irrigation water would be needed per m^2 of land per year, respectively.

The source of irrigation water is already available at low cost within SIA as the treated effluent from the wastewater treatment facility. Cost of treating this water is estimated at about KD. 0.262 per m^3 compared to KD. 0.65 per m^3 for fresh water.

The general cost function representing the total annualized cost is given as:

$L_i = a_i + b_i T$ for $i = 0, 1, \text{or } 2$

where

L_i = the annualized total cost for any irrigation scenario, KD/yr

T = the annual waste input t/yr.

The total annualized cost includes the capital as well as the operation and maintenance costs. The capital cost considered the cost of infrastructure, irrigation system, mechanical equipment, and civil works. The operation and maintenance cost takes into account the cost of water needed for irrigation, power, labor, fertilizer, and equipment maintenance.

Since the land is owned by the government and the landfarming technology is meant to reclaim this land, it was decided to exclude the land rental cost from our analysis. The annual rental charge equals 0.075 KD/m^2.

Excluding cost of land rental charge and adjusting for the cost savings due to the use of treated effluents instead of fresh water, the total cost (L_i) becomes

$L_i = a_i + b_i T - 0.075 A - (0.65\text{-}0.262)i A/N$

for i=0, 1, or 2

where

A = the area to be landfarmed, m^2

N = the degradation period, yr.

For the purpose of the cost analysis, the second scenario was considered (i=1). In addition, the following values were substituted into the above function.

$T = 53{,}000$ t/yr; $a_i = 158127$; $b_i = 5.559$

$A = 2{,}100{,}000\ m^2$; and $N = 10$ years.

The substitution results in the total annualized cost L_1= KD. 213,134

A simple mathematical model was developed to estimate the preliminary mix requirements of various components. This linear model ensure the complete utilization of oily sludge as a primary objective, and includes the proper ratios of: sludge with 25% oil; water at least 72.5%; and nitrogen about 2%. The model results indicate that, given the waste types available, Table 3, the landfarming option utilizes:

o The full yearly amount of oily sludge (as desired) including 30,000 t/yr and 30,000 t/yr (approximately) of oil and water respectively.

- About 90,000 t of ammonia water and the corresponding amount of 1,800 t of nitrogen generated from fertilizer factory of Petrochemical Industries Company (PIC) situated in the SIA.

Additional nitrogen and fertilizers might be needed which costs KD. 5,625. This includes cost of fertilizer, aeration and spreading equipment.

Table 3. Landfarming Technical Parameters

Technical Parameters	Parameter Value
I. Potential Wastes for Landfarming	
*Oily semisolid wastes	
-Ammount (t/yr)	60,000
-Amount of oil (t/yr)	30,000 (assuming 50% oil)
*PIC ammonia water	
-Amount (t/yr)	150,000
-Amount of nitrogen (t/yr)	3,000 (assuming 2% nitrogen)
II. Other Potential Landfarming Requirments*	
*Ammounts of irrigation water (t) from MEW or Shuaiba Wastewater Treatment Plant	Depend on the actual need under local conditions
*Fertilizers:	
-Additional nitrogen (t/yr)	700
-Phosphorous (t/yr)	300
-Potassium (t/yr)	350
*Soil and environmental requirements:	
-Area requirments (hectares)	200 or 20/yr
-Depth of falling (cm)	10-30
-pH range	6-8
-Maximum oil allowed in soil (%)	10
-Temperature range	Kuwait ambient temperature

* To be optimized under local conditions

Transportation Costs. One of the primary concerns of the analysis is to study the impact of transportation cost on the selection of the optimum waste handling method. The study comprises the cost calculation of transportation for a distance of 10-60 km by pipelines and tankers. The amount of wastes is determined by the generators but the additional waste material needed for the landfarming technology is given on a preliminary engineering design basis.

A comparative cost analysis resulted in the following annualized cost estimates for pipelines and tankers to transport the PIC water.

	Tankers	Pipelines
Annualized Capital, operating and maintenance cost, KD	165,000	122,750

The above costs are also annualized based on 8% discount rate over twenty years. Clearly, the pipeline option costs less than tanker vehicles. Therefore, pipeline transportation of PIC water is selected. The estimated cost of transporting oily sludge to the landfarming site is KD. 142,750.

Transportation costs for water and other wastes are combined with the facility cost, assuming the site is 60 km south of the source of generating oily waste. Thus the total annualized landfarming costs with irrigation level of 1 m^3/m^2 will be:

213,134 + 122,750 + 142,750 = KD. 478,634

Based on the preceding analysis, the costs of handling oily waste using landfarming or incineration are summarized in Table 4.

Table 4. Summary of costs for incineration and landfarming

Treatment	Total Annualized Costs, KD		
	Facility	Transportation	Total
Incineration	720,000	47,126	767,126
Landfarming	213,134	265,500	478,634

The preceding cost analysis indicates that the landfarming presents a savings of more than KD. 287,000 which is about 37.5% of the total incineration cost per year. Moreover, the primary advantage of landfarming is that it might provide more than 200 ha of cultivable land, which contributes to the agricultural development in Kuwait.

ACKNOWLEDGEMENT

This work is part of a project which was funded by the Shuaiba Area Authority (SAA) and Kuwait Institute for Scientific Research (KISR).

The authors extend their sincere thanks and gratitude to their colleagues in KNPC, KOC, Environmental Protection Centre in SAA, and in Biotechnology, Environmental Science, and Applied Systems Departments in KISR for their input and help during the execution of the project.

REFERENCES

Arora, H.S., R.R. Cantor and J.C. Hemeth. 1982. Land treatment: A viable and successful method for treating petroleum industry wastes. *Environmental International* 7:285-291.

Bonnier, P.E., G.L. Akoun, E.C. Cadron, E.D. Edwards, and W. Hocknell. 1980. Sludge farming: A technique for the disposal of oily refinery wastes. Cancawe Report No. 3/80, Hague Netherlands.

Brown, K.W., H. Brawand; J.C. Thomas, and G.B. Evans. 1982. Impact of stimulated land treatment with oily sludges on Ryegrass emergence and yield. *Agronomy Journal* 74(2):257-261.

ElNawawy, A.S., K. Puskas, F. Ghobrial and A. Elimam. 1986a. Waste management program for the Enlarged Shuaiba Industrial Area. Kuwait Institute for Scientific Research, KISR Report No. 1918, Kuwait.

ElNawawy, A.S., K. Puskas, A. Elimam, D. Al-Bakri, and M. Allam. 1986b. Solid waste management program for the Enlarged Shuaiba Industrial Area . Kuwait Institute for Scientific Research, KISR Report No. 2061, Kuwait.

Hornick, S.B., R.H. Fisher and P.A. Paolini. 1983. Petroleum wastes. In *Land Treatment of Hazardous Wastes*. Edited by J.F. Parr, P.B. Marsh, J.M. Kla. Park Ridge, N.J.: Noyes Data Corporation.

Phung, H. and D.E. Ross. 1978. Soil incorporation of petroleum waste. *Water 75*.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

TREATMENT OF TOXIC WASTEWATERS BY POWDERED ACTIVATED CARBON

John Meidl

ZIMPRO/PASSAVANT INC.
301 W. Military Rd. - Rothschild, WI 54474

ABSTRACT

In today's climate, total treatment of toxics - liquids and solids - is becoming more common due to impending regulations and the price tag associated with solids disposal.

The use of powdered carbon may be able to solve treatment problems associated with toxics, and alleviate or eliminate the exorbitant price tag associated with toxic solids disposal.

By operating a powdered carbon enhanced activated sludge system (PACT™), efficient treatment of toxics will occur, and sludge quantities to disposal can be reduced. Treatment of toxics is documented at PACT installations at DuPont, Ciba-Geigy, and Lomac, among others. Savings on solids to disposal is best illustrated by comparing activated sludge and the same system upgraded with powdered carbon.

	Activated Sludge	PACT™
Biosolids, lb/d	500	500
Carbon, lb/d	0	250
Total, ton/yr	91	137
Wet Cake to Disposal, ton/yr	610	340
Annual Cost, $		
Carbon @ $.40/lb	0	$36,000
Disposal @ $200/wt. ton	$122,000	$68,000
Total	$122,000	$104,000

Currently, on-site recovery of the carbon (and destruction of the toxics) isn't feasible until about a ton of carbon per day is being used. Cost data shows that, depending on the price of carbon and the cost of solids disposal, a ton-per-day regeneration system can pay for itself within two years. Anasysis of the 10 gpm skid wet air regeneration system at Lomac's PACT facility shows carbon recoveries to be greater than 95% with skid operating costs being about $.05/gal spent carbon processed.

When PACT is compared to other adsorptive methods like GAC to treat wastewater, PACT will generally show a significant cost advantage. An example is treatment of Stringfellow quarry leachate. Carbon requirements of PACT and GAC to treat similar levels is < 700 mg/l vs. > 7,000 mg/l respectively. Though capital costs are similar, annual O&M costs for PACT is $435,000; for GAC these costs exceed $2,000,000.

Presentation of Entire Paper at Conference, Monday, September 28, 1987.

The session will analyze PACT's ability to treat toxics, to control TTO's, and to ensure compliance in effluent bioassay testing. It will also discuss PACT case histories related to RCRA and CERCLA projects and give cost figures related thereto.

****

WHERE ENTIRE PAPER HAS NOT BEEN INCLUDED IN THESE PROCEEDINGS COPIES WILL BE AVAILABLE IN THE CONFERENCE LOBBY.

THE ATTENUATION OF LANDFILL GAS ODOUR USING WASTE MATERIALS

J R Emberton, P E Scott and C G Dent
Environmental Safety Centre
AERE Harwell
UK

ABSTRACT

Odour from landfill gas is probably responsible for the largest number of complaints made to both landfill operators and regulators in the UK. This paper describes a laboratory and field research programme funded by the UK Department of the Environment (DoE) which has investigated the effectiveness of waste materials to attenuate landfill gas odour. A total of twenty-two materials have been studied in the laboratory, at various moisture contents. From the findings of the laboratory programmes, three individual materials and three mixtures were selected for field trials at a landfill in Essex, UK. These materials were emplaced in trenches excavated through the landfill cap. The odour of the gas detected at three depths within the attenuating material was monitored, on a monthly basis, for two years. The results of the laboratory and field trials, along with possible attenuation mechanisms, are presented.

INTRODUCTION

The aerobic and anaerobic decomposition of domestic and commercial wastes disposed of to landfill inevitably leads to the production of highly odorous landfill gas (9). The odour associated with this gas is a very common cause of public complaint and may pose a significant environmental problem (7).

The odorous nature of the gas results from the presence of certain trace organic compounds (14). These compounds may be released by the processes of direct volatilisation, chemical reaction or microbial degradation of the waste. Past research has identified over 120 individual compounds present at trace levels within landfill gas. Of these compounds, approximately 10% are usually responsible for odour (14, 15). Various organic groups including the esters, organosulphur, cyclic and aromatic compounds are of particular importance. These compounds are commonly detected in concentrations at which they impart a significant odour. The characteristic odour of a particular landfill gas will be dependent on a combination of distinctive odours. The contribution of each individual component to the overall odour will depend on the concentration at which it is present and the odour threshold for that particular compound.

The composition of landfill gas, including that of the trace compounds factors, including the nature of the waste deposited, the age of the waste, and the nature and extent of microbial activity taking place. As degradation of the waste proceeds with time, the odour of the landfill gas released will alter, reflecting changes in the gas composition. Research has suggested that different organic groups will influence the odour of the landfill gas at varying stages of the degradation process (13,16).

Empirical observations at landfill sites have shown that odour problems may be reduced by the application of certain cover materials. In such applications the principal components responsible for the odour at any particular stage of refuse degradation are attenuated as they pass through the cover material.

The ability of a material to attenuate landfill odour will be dependent upon various factors. Those characteristics which might be expected to optimise this ability include:

i) a high surface area:volume ratio (specific surface area);
ii) the presence of active sites capable of attenuating the odorous trace components.
iii) active sites which are not susceptible to oxidation or surface blinding.

It is also important that the material can easily be handled and that adequate supplies exist. The material will need to be utilised in a manner that allows the even passage of the landfill gas.

The mechanisms involved at the active sites referred to above are not clearly understood but may be physical (e.g. absorption and adsorption), chemical or biological. Some work is currently being undertaken on identification of active sites and determination of mechanisms of attenuation. The results of this work are not included in this paper.

OBJECTIVES

The present programme of research is jointly funded by the UK Department of the Environment and Essex County Council. The project was designed to investigate the potential use of a wide range of materials to attenuate the odour of landfill gas. A particular feature of the programme was the selection of materials which were themselves wastes and which could therefore be applied at low cost. Materials found to display good odour attenuation characteristics could be used primarily as intermediate cover materials during operation or could be incorporated into a passive gas venting system.

METHODS

Laboratory Experiments

An initial laboratory programme was designed to screen a wide range of materials for their ability to attenuate landfill gas odour. One of the purposes of this programme was to identify individual materials, or mixtures of materials, for subsequent large scale field experiments at a six hectare landfill site at Ugley in Essex, UK.

A total of 22 individual materials and ten mixtures were tested in the laboratory (Table 1). A known weight of each material was placed in a sintered funnel. In addition to dry samples, tests were also carried out on each material with a known volume of water added to achieve moisture contents of 20% and 40% v/v. The moistened samples were then re-homogenised before use.

The sintered funnel was placed into the apparatus shown in Figure 1. With the Polytetrafluoroethylene (PTFE) lined 3-way tap positioned to bypass the sintered funnel, a constant gas flow was set using the needle valve on the cylinder. The

3-way tap was then adjusted to allow landfill gas to pass through the sample. The flow rate was measured and the time taken for the first odour breakthrough noted. This time can be defined as the 'odour breakthrough period' i.e. the period which elapses before any component or components can be detected at concentrations above their odour threshold. Experiments were repeated using an odour panel, made up of a number of scientists, to achieve comparative data.

Observations by the panel were quantified by an index developed for this purpose and referred to as the Waste Research Unit Odour Index (WRUOI). The WRUOI is defined as the ratio of material volume to volume of gas required to cause odour breakthrough. Thus a WRUOI of 2.00 means that a 1 cm column of material will attenuate 2 cm of landfill gas.

The results some of the laboratory tests are given in Figure 2. A more detailed account of the laboratory trials is available in an HMSO document (6).

Table 1. List of individual materials and mixture, tested in the Laboratory.

Individual

West Thurrock pulverised fuel ash
West Thurrock furnace bottom ash
Ratcliffe pulverised fuel ash
Ratcliffe furnace bottom ash
Didcot pulverised fuel ash
Pembroke oil grit
Edmonton incinerator ash
Arsenical slag
Soda lime
Agricultural lime
Buxton lime
Oolitic limestone
Thanet sand
Raised ballast
Pea shingle
Uttlesford topsoil
Harwell topsoil
Rufford colliery shale
Brick dust
Sawdust
Wood Chippings
Ground newspaper
Charcoal

Mixtures

Newspaper:colliery shale	(10:90)
Sawdust:Didcot PFA	(20:80)
Sawdust:Incinerator ash	(20:80)
Newspaper:Incinerator ash	(10:90)
Sawdust:Colliery shale	(20:80)
Newspaper:Didcot PFA	(10:90)
Colliery shale: Thanet sand	(50:50)
Incinerator ash:Didcot PFA	(50:50)
Uttlesford topsoil: Incinerator ash	(50:50)
Ballast:Didcot PFA	(75:25)
Ballast:Didcot PFA	(50:50)

Field Trials

From the results of the laboratory trials (discussed later) and taking into consideration availability and physical stability, then three individual materials and three mixtures were selected for subsequent field trails at the Ugley landfill. These were:

Trench 1: Uttlesford topsoil
Trench 2: Rufford Colliery shale
Trench 3: Edmonton Incinerator ash
Trench 4: Edmonton Incinerator ash and sawdust (80:20)
Trench 5: Rufford Colliery shale and sawdust (80:20)
Trench 6: Didcot Pulverised fuel ash and sawdust (80:20)

Six trenches (10m long by 2m wide by 1.1m deep) were excavated through the clay cap to the surface of the refuse below. The trenches were located in an experimental area towards the eastern boundary of the site. Materials were placed in the trenches as received, i.e. the moisture content and particle size distribution were not altered prior to placement. Since the weather was fine during the period of excavation, then the materials were dry on placement.

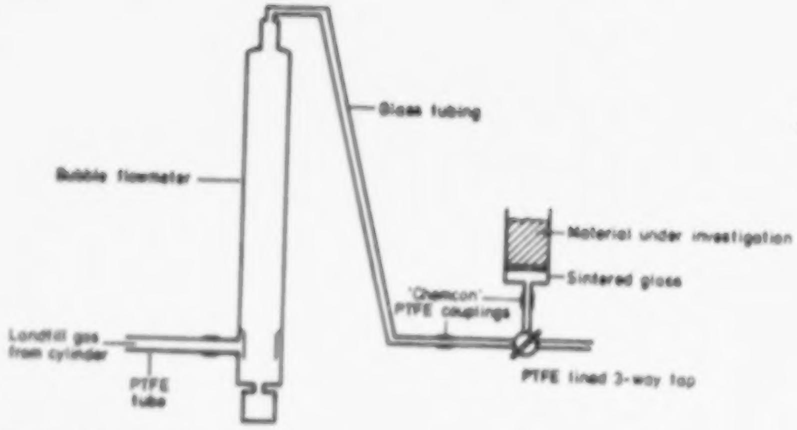

Glass tubing
Bubble flowmeter
Material under investigation
Sintered glass
'Chemcon' PTFE couplings
Landfill gas from cylinder
PTFE tube
PTFE lined 3-way tap

Fig. 1 Diagram of laboratory apparatus used to investigate odour attenuation by waste materials

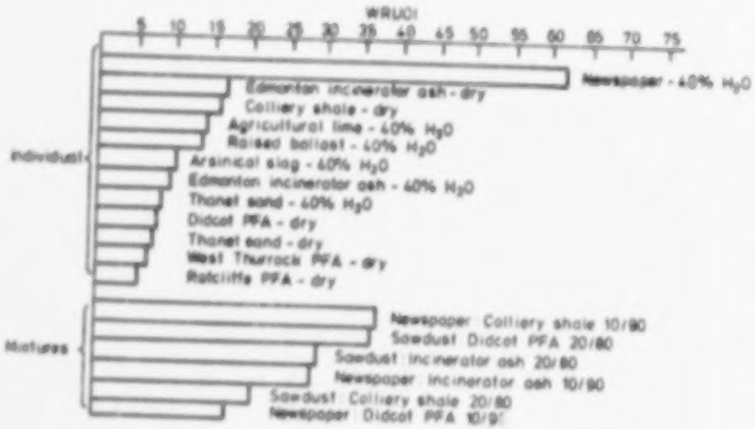


Fig. 2 Histogram of WRUOI of individual components and mixtures

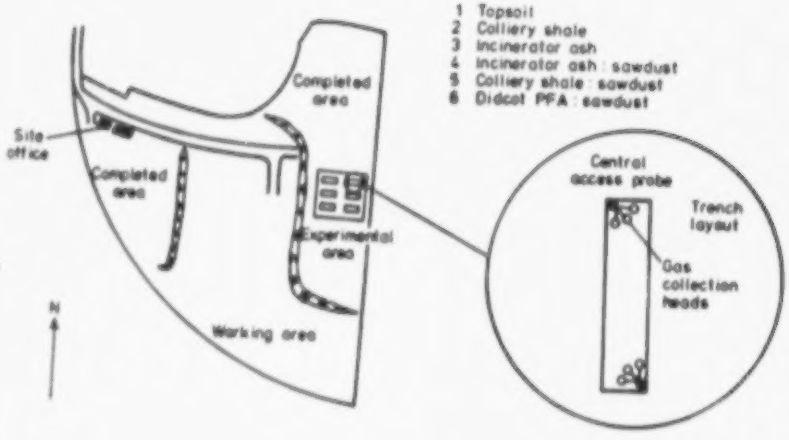

1 Topsoil
2 Colliery shale
3 Incinerator ash
4 Incinerator ash : sawdust
5 Colliery shale : sawdust
6 Didcot PFA : sawdust
Completed area
Site office
Completed area
Experimental area
Working area
N
Central access probe
Trench layout
Gas collection heads

Fig 3 Map of site with inlay of collection head layout in trench

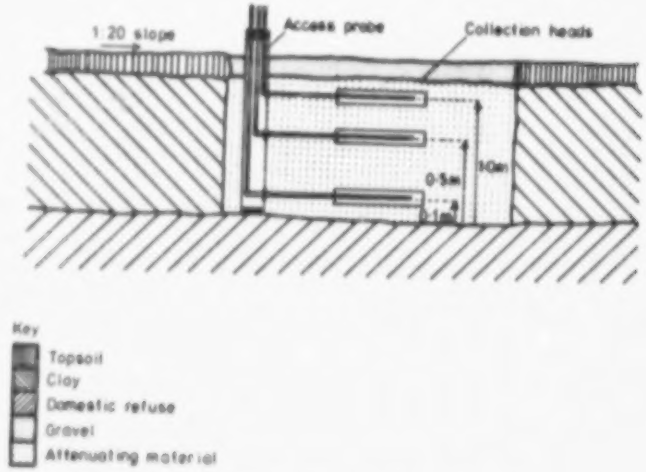

1:20 slope
Access probe
Collection heads
1·0m
0·5m
0·1m
Key
Topsoil
Clay
Domestic refuse
Gravel
Attenuating material

Fig 4 Cross section of one trench

Two sets of PTFE probes were placed in diametrically opposed corners of each trench during filling (Figures 3 and 4). Each set comprised 3 separate probes and each probe was connected to its own collection head. The collection heads were laid horizontally in a gravel bed at depths of 0.1m, 0.5m and 1.0m and at a distance of 2.5m from the vertical section of the probe (Fig 4). Each collection head was offset so that gas collected by one probe would not influence that collected by adjacent probes.

Monitoring of all 36 PTFE probes was conducted on a monthly basis during which the odour emitted from each was characterised by an odour panel as with the earlier laboratory experiments.

The odour detected in each of the probes was classified into one of four broad groups. These were:

i) no odour detected;
ii) a sweet odour;
iii) a bitter acrid odour;
iv) an odour indistinguishable from the unattenuated landfill gas detected in control probes.

In addition any other easily identifiable odours were noted.

Factors such as ambient temperature, and barometric and gas pressures were also noted during each visit.

Collection and Analysis of Landfill Gas Samples

In order to gain some indication of those trace compounds present in the landfill gas generated at Ugley and which might be responsible for the odours observed, samples of the gas were recovered from 4m below the surface of the experimental area. The sampling methodology involved was developed by the Waste Research Unit at Harwell and has been published in detail elsewhere (2). A brief description only is given here.

The landfill gas samples were recovered using the apparatus shown in Figure 5. A metal piezometer was driven into the waste to a depth of 4m. The landfill gas was drawn from the waste to the sampling apparatus using a 12 volt battery driven diaphragm pump via small bore PTFE tubing. Components of the sampling apparatus were restricted to PTFE, glass and metal in order to minimise the adsorption or absorption of trace compounds and the release of any compounds into the gas stream from components of the apparatus.

Landfill gas samples of known volume were collected in condensate traps and on Tenax and Porapak Q trapping media and analysed for trace components by GC/MS techniques. A second set of samples was collected on Tenax for the analysis of organo-sulphur compounds only. A GC spectrophotometric technique was used for analysis of both the organo-sulphur compounds and for hydrogen sulphide from additional samples collected separately in stainless steel gas bombs.

Problems Encountered

1. Laboratory Experiments

All of the materials under investigation were tested in a series of individual experiments. During the course of the laboratory programme, it became apparent that a number of the materials possessed physical properties which limited their ability to attenuate odour during certain circumstances. The PFA samples all gave an above average WRUOI when dry. However when slightly moist (20% moisture), they rapidly coagulated into lumps; at a moisture content of 40% they formed a slurry which subsequently set into a solid mass of very low gas permeability. During experiments on these samples, gas pressure built up below the sintered funnel and this eventually forced the ejection of the samples from the apparatus or produced blow holes through which the pressure was relieved.

The laboratory experiments involving moist incinerator ash and moist colliery shale reproduced similar problems to those experienced with the moist PFAs. Although of a much lower magnitude than with the moist PFA samples, these problems nevertheless had a marked influence on odour attenuation efficiency. In order to overcome these physical difficulties whilst retaining their attenuating properties, these materials were admixed with a second material which preferentially absorbed water providing a porous support. The use of these mixtures successfully overcame the problems previously encountered.

2. Field Experiments

Intermittent flooding during the winter period of the experimental trenches proved a major problem during the field trials. The flooding, ten months into the experimental programme, was at least in part caused by the final restoration of the area immediately adjacent to the trenches. Deposition of a layer of topsoil produced a downward gradient allowing migration of water into the trenches. It is now planned to install an extensive network of land drains around the experimental area in order to negate this problem.

RESULTS

1. Laboratory Experiments

All individual experiments were terminated on odour breakthrough. The results for the WRUOI ranged from 0.63 for pea shingle to 62.4 for moistened ground newspaper. Figure 2 presents the results for the six best dry and six best wet (40% moisture) individual materials. Values are also given for some of the mixtures investigated. The mean WRUOI is presented where duplicate results were obtained. Although the index for charcoal was very high, this was included for comparative purposes only and therefore the result is not included in Figure 2. It should be noted however that the highest WRUOI shown in Figure 2, ie that for the ground newspaper at 40% moisture content, was nevertheless still a factor of six below that of dry charcoal.

In all cases, excluding that with pea shingle, the odour of the landfill gas was modified by passage through the sample, suggesting that odorous components were being attenuated. The odour on break-through varied with the material tested indicating that the same trace components were not being attenuated in each case.

The pulverised fuel ash (PFA) samples, when dry, all gave results above the mean WRUOI calculated from the total range of 22 materials. This may be related to its pozzolanic properties. In addition PFA has a high specific surface area over which attenuation may occur and there appears to be a direct relationship between its carbon content and the WRUOI (6). PFA also contains significant amounts of iron oxide (3) which is reported to be effective at attenuating the odour of the particularly pungent sulphurous compounds (5). The Furnace Bottom Ashes (FBAs) gave lower WRUOIs, reflecting perhaps their lower specific surface area and reduced carbon content. When wetted, the attenuation efficiency of the FBAs was slightly increased which may reflect the dissolution of an inhibitory surface film from active sites or simply enhanced chemical or physical sorption of odorous species. The attenuation efficiency of water itself was shown to be negligible.

Incinerator ash also contains a significant proportion of carbon and iron oxide and has a high specific surface area. This is reflected by its WRUOI of 16.71 although this was reduced by the addition of moisture. The arsenical slag gave an improved performance when wet which may reflect the dissolution of a surface film of alkali metal exposing active sites or again enhanced chemical or physical sorption. The effectiveness of the alkali materials such as the agricultural lime may be due to calcium oxide hydrating to form calcium hydroxide. This material is used industrially to remove sulphur dioxide and may also have an affinity for organo sulphur compounds.

The significant attenuating properties of the Thanet sand, topsoils and raised ballast samples may be due to the clay minerals which these materials contain. Clay minerals have been shown to be effective at attenuating odour, particularly those minerals which contain a large fraction of montmorillonite such as Thanet sand (12).

Colliery shale exhibited similar odour attenuating properties to incinerator ash. Although ground newspaper when dry gave a low WRUOI, its effectiveness was increased by the addition of water which tended to promote a more even movement of gas through the sample. A similar though less dramatic situation was observed with sawdust. Both of these materials also gave off a resinous "woody" odour which may have masked the odour of certain trace components. This would have effectively delayed the point of apparent odour breakthrough which in turn would have produced an artificially high WRUOI.

With wet samples, the mixtures of PFA, colliery shale and incinerator ash with both newspaper and sawdust exhibited superior permeability to the individual materials. These mixtures also showed significant potential for odour attenuation. By comparison, results for mixtures containing materials such as topsoil, Thanet sand and raised ballast were not as encouraging and were not pursued further.

2. Field Experiments

The laboratory trials produced a selection of materials and mixtures for use in large scale field trials.

In the laboratory trials, clear differences between the six materials were seen in terms of their odour attenuating capabilities (6). In these experiments, the materials were homogeneous in terms of moisture content, and all were dried, ground and sieved to a standard size. Also, both the gas flow and pressure were maintained at constant levels throughout. Although the results achieved were valuable in determining relative performance, the controlled conditions of the laboratory experiment did not represent those found in the field. Hence, in the field experiments, both landfill gas pressures and methane concentrations were found to vary over the experimental period. Moisture contents also varied substantially.

The results of the field trials are summarised in Figure 6. From the figure, it can be seen that the relative performance of each of the individual materials is quite close (much closer than was seen in the earlier laboratory trials). There is however a marked contrast between the performance of the individual materials and the mixtures, with all mixtures exhibiting much better odour attenuation properties than any individual material.

Again from Figure 6, breakthrough of a sweet odour was observed to have occurred within two months of placement for at least one collection head within each of the trenches containing individual materials. (see

Fig 6). Breakthrough of a more bitter, acrid, odour was detected during the fourth, fifth and sixth months for the topsoil, colliery shale and incinerator ash respectively. Breakthrough of the bitter odour in the upper collection heads was only detected in one probe (probe 6) on one occasion.

For the trenches containing mixtures, then in all eighteen installed collection heads, an initial woody resinous odour was noticed. In the case of the incinerator ash:sawdust and PFA:sawdust mixes this characteristic odour pervaded all collection heads for a period of two months, masking any other odours that may have been present. In the two sets of probes within the colliery shale: sawdust trench this odour only persisted for one month, except for the lowest collection head in probe 10 where it was detected over two months. Break- through of the bitter odour in the lowest collection heads of all trenches containing mixtures had occurred by the ninth month following emplacement, except in probe 10, where the bitter odour was never detected. Because of the subsequent flooding problems (referred to earlier), no further comparison of performance can be made following the ninth month. For this reason, a relative assessment has been based on the "sweet odour profiles" only which from Figure 6 suggest the colliery shale:sawdust mix to be marginally more effective than the PFA:sawdust mix which in turn is more effective than the incinerator ash: sawdust mix. Both the latter mixes performed much better than the relevant individual material. It is interesting that the results of the earlier laboratory trials (6) suggested sawdust had only a moderate WRUOI when both wet and dry. This suggests that the enhanced odour attenuation characteristics of the mixtures does in fact derive from the role of sawdust as a porous support rather than from its own attenuation properties.

The results of both field and laboratory experiments suggest complete attenuation of odour will be achieved for only a number of months before breakthrough of odour begins to occur. Assuming a WRUOI of 20 and a gas production rate of 0.01 m^3/ tonne/d (based on a yield of $40m^3$ of gas/tonne over 10 years) then a 0.1m layer of attenuating material laid over a 2m lift of refuse (compacted to 0.65 tonne/m^3) would achieve complete attenuation of odour for a period of 5 months. Of course, gas production rates are not uniform and are much lower in the early period after deposit of the waste. Assuming an initial gas production rate of $0.0025m^3$/tonne/d, then with the same material, complete attenuation would be achieved for a period of nearly two years. Whilst this was not observed at the Ugley site, the trenches here overlay waste which is approximately four years old where gas production rates are nearer to $0.01m^3$/tonne/d. The most objectionable odours (often associated with organosulphur compounds) are usually associated with the period during and immediately following deposit of refuse. Hence, even when complete attenuation is only achieved for a number of months, the benefit in terms of odour control is likely to be significant.

GCMS Analysis

A total of 84 individual compounds were identified at trace levels in the landfill gas samples retrieved from the Ugley landfill site. Of these, 24 were found in concentrations in excess of their odour thresholds. The odour thresholds were compiled using as reference sources ASTM data (1) and two other tests (10,11). Reported thresholds are sometimes expressed as a range of values which reflect variations in the response of different individuals to the same odour (known to vary by at least an order of magnitude). Hence a review of the literature has produced a range of threshold values (Table 2) which reflects both the above and the variation from compiling data from different sources. The threshold for each compound has been adopted following an assessment of the relative degrees of confidence which can be placed on the data from each source. The data presented in Table 2 show the ten most odorous compounds present in the landfill gas and the dilution factors required to reduce these compounds to levels below their individual odour thresholds. The dilution factors provide a means of directly comparing the relative contribution of each individual component to the overall odour.

The composition of the odorous fraction of the landfill gas at Ugley is dominated by the presence of esters which usually have a sweet or fruity odour. The "sweet" odour encountered throughout the field trials is therefore probably due to the breakthrough and passage of esters through the cover materials. Ethyl butanoate is by far the most odorous component of the gas and would require a dilution in excess of 23,000 times in order to negate its odour. The only organosulphur compound of significance is dimethyl sulphide. Sulphur compounds characteristically posses a strong pungent odour and are usually present in very high concentrations during the early phases of refuse degradation. Since the refuse immediately below the experimental trenches at Ugley is approximately four years of age, high levels of organosulphur would not be expected. Limonene is a cyclic organic compound frequently detected in landfill gas at concentrations in excess of its odour threshold. It has a tart bitter odour and is present at significant levels in the landfill gas from Ugley. The "bitter" odour reported during the field trial may therefore be due to the presence of significant concentrations of limonene and dimethyl sulphide in the landfill gas.

Future work will include a further gas sampling run during which samples will be collected from below one of trenches and at varying depths within it. The analysis of these samples should provide a more clear identification of those trace components responsible for the characteristic "sweet" and "bitter" odours reported from field trials and provide a much clearer understanding of the effectiveness of each material or material mix in attenuating specific trace components.

CONCLUSIONS

The research programme has demonstrated that the odour of landfill gas can be initially attenuated and subsequently modified as a result of its passage through certain materials. The attenuation process is dependent on a number of factors. Chemical composition (for example the presence of carbon or iron oxide) and particle size appear important. Moisture content is certainly an important factor. Further work however is required to investigate the actual mechanisms involved.

Results achieved from field trials were not as conclusive as those from laboratory experiments. This is probably due to the much more variable conditions in the field and the relatively long periods between monitoring in the field experiments as compared to the laboratory tests. Nevertheless, all the materials tested in the field experiments exhibited some capacity to attenuate the odour of landfill gas, with the performance of the individual materials being considerably enhanced when mixed with sawdust.

Even for the most successful materials, the results of both field and laboratory experiments suggest that in a typical situation, odour will only be completely attenuated for a number of months before breakthrough occurs. Nevertheless, their application as interim cover materials will provide considerable benefit with regard to odour control during the landfilling operation itself, which is the period during which most complaints occur. Furthermore, since the materials studied are themselves wastes, then their local availability would ensure this benefit was achieved at little or no cost.

ACKNOWLEDGEMENTS

This work has been funded by the UK Department of the Environment (DoE). The authors wish to thank members of the DoE's Land Wastes Division for their advice and assistance.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Table 2. Ten Most Odorous Compounds Detected in Landfill Gas from Ugley Landfill. Their Concentration, Odour Threshold and Dilution Factor Required to Reduce These Concentrations Detected Below the Odour Threshold.

Compound	Concentration observed in landfill gas from Ugley landfill mg/m^3	Odour Thresholds mg/m^3		Dilution factor required to reduce concentration below odour threshold
		Value Adopted	Range Reported	
1. Ethyl butanoate	70	3×10^{-3}	3×10^{-3} - 0.04	23,333
2. Methyl butanoate	15	5×10^{-3}	9×10^{-3} - 1×10^{-3}	3,000
3. Dimethyl sulphide	24	1×10^{-2}	6×10^{-4} - 0.6	2,400
4. Limonene	129	5.7×10^{-2}	5.7×10^{-2}	2,263
5. Hexenes	11	8×10^{-2}	8×10^{-2}	1,375
6. Butan-2-ol	105	1×10^{-1}	0.05 - 50	1,050
7. Propyl butanoate	35	1×10^{-1}	1×10^{-1}	350
8. Ethyl propionate	22	1×10^{-1}	-	220
9. Propyl propionate	21	1×10^{-1}	-	210
10. Toluene	68	1×10^{-1}	0.6 - 100	97

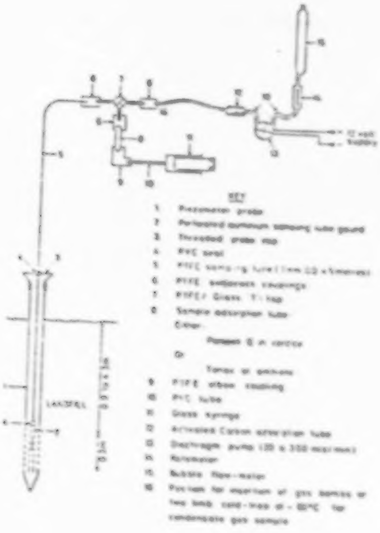

12 volt supply
LANDFILL
KEY
1 Piezometer probe
2 Perforated aluminium sampling tube guard
3 Threaded probe cap
4 PVC seal
5 PTFE sampling tube
6 PTFE swagelock couplings
7 PTFE/Glass T-tap
8 Sample adsorption tube
Either
Porapak Q in series
Or
Tenax
9 PTFE elbow coupling
10 PVC tube
11 Glass syringe
12 Activated Carbon adsorption tube
13 Diaphragm pump
14 Rotameter
15 Bubble flow-meter
16 Position for insertion of gas bombs or two bulb cold-trap for condensate gas sample

Figure 6 Schematic Diagram Of Sampling Apparatus

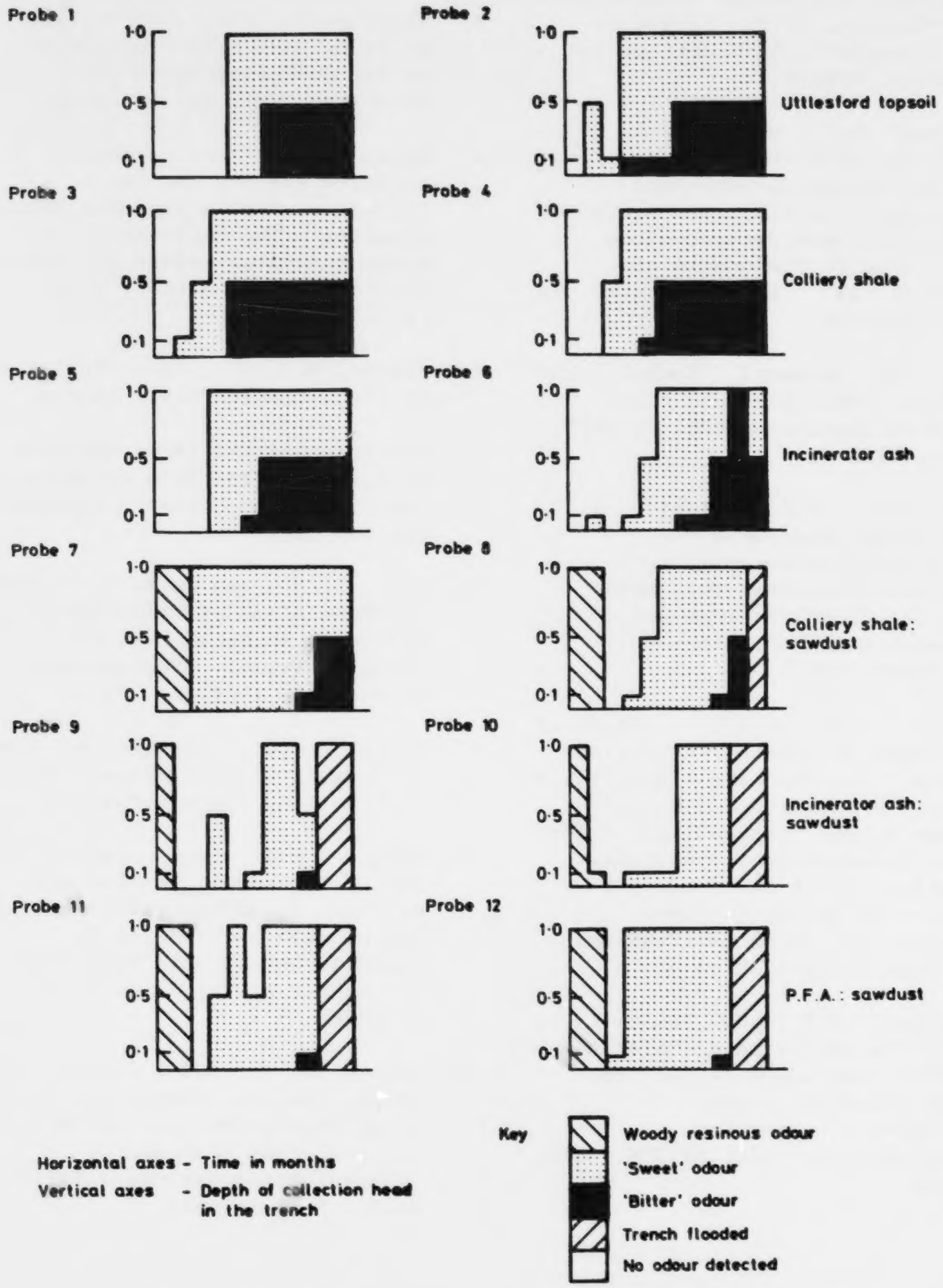


Fig 6 Odour detected in the probes during the experimental period.

REFERENCES

1. American Society for Testing Materials (ASTM), Committee E-18 on Sensory Evaluation of Materials and Products, 1978. Edited by F A Fazzalari, ASTM data series DS 48A 05-048010-36.

2. Brookes, B.I. and Young, P.J., 1983, The Development of Sampling and Gas Chromatography-Mass Spectrometry Analytical Procedures to Identify and Determine the Minor Organic Components of Landfill Gas. Talanta, Vol 30, No 9, pp 665-676.

3. Coal Ash Disposal Manual, 2nd Edition, 1981, Electric Power Research Institute. EPR1 CS 2049 project 1685-3.

4. Dietzmann, H.E. et al, 1979, Analytical Procedures for Characterising Unregulated Pollutant Emissions from Motor Vehicles. USEPA Environmental Sciences Research Laboratory, EPA-600/2-79-017.

5. Eikum, A.S, 1983, Study of Processes in View of Preventing Odours. In L'Hermite P and Ott, H (Eds). Processing and Use of Sewage Sludge. Proceedings of the Third International Symposium, Brighton, 27-30 September 1983. Commission of the European Communities. D Reidel Publishing Co. ISBN 90-277-1727-3.

6. Emberton, J.R. and Young, P.J., 1985, The Use of Cover Materials to Attenuate Landfill Gas Odour at Ugley Landfill, Essex. I Preliminary Laboratory Investigation. AERE R11736, HMSO London.

7. Fletcher, P., 1987, Charactersation of Forty UK Landfill Sites. MSc Thesis. Brunel University, London.

8. Mindrop, R., 1978, The Analysis of Gases and Light Hydrocarbons by Gas Chromatography. J Chromatog. Sci. Vol 16, p 380.

9. Rees, J.F. and Viney, I., Leachate Quality and Gas Production from a Domestic Refuse Landfill. The Implication of Water Saturated Refuse at Aveley Landfill. AERE R10328, HMSO London.

10. Summer, W., 1971, Odour Pollution of Air. Leonard Hill, London.

11. Verscheurei, K., 1977, Handbook of Environmental Data on Organic Chemicals. Van Nostrand Rheinhold Co, New York.

12. Weir, A. H., and Catt, J.A (1968) The Mineralogy of Palaeogene Sediments in North East Kent (Great Britain). Sedimentary Geology, 3, 1969, pp 17-33.

13. Young, P.J., Parker, A. and Brookes, B.I, 1982, Unpublished Information. AERE Harwell.

14. Young, P.J. and Parker, A., 1983a, The Identification and Possible Environmental Impact of Trace Gases and Vapours in Landfill Gas. Waste Management and Research, Vol 1, No 3, pp 213-226.

15. Young, P.J. and Parker, A., 1983b, Vapours, Odours and Toxic Gases from Landfills. ASTM International Symposium, Industrial and Hazardous Solid Waste, Philadelphia.

PLASTIC CONCRETE SLURRY TRENCH CUTOFF WALLS

Jeffrey C. Evans
Assistant Professor
of Civil Engineering
Bucknell University
Lewisburg, PA 17837

Eric D. Stahl
Research Director
R. H. Stahl & Sons, Inc.
Sunbury, PA 17801

Eric Drooff
Project Engineer
Sardone Construction Co.
Parsippany, NJ 07054

ABSTRACT

The studies revealed that plastic concrete can be prepared having a coefficient of hydraulic conductivity that is less than 1×10^{-7} cm/sec. Further, the shear strength of the material is greater than that of soil-bentonite or cement-bentonite. Plastic concrete appears to offer greater resistance to degradation in response to permeation with contaminant pore fluids. Considering the possible advantages of slurry trench cutoff walls of plastic concrete in terms of minimizing construction defects, minimizing hydraulic fracturing potential, and greater resistance to degradation due to contaminants, it is concluded that plastic concrete offers a technology that should be given consideration in the future where vertical barriers are required.

INTRODUCTION

The remediation of waste disposal sites frequently requires the use of a vertical barrier to minimize the influx of uncontaminated groundwater into the site, minimize the offsite migration of contaminated groundwater, and/or minimize groundwater pumpage and treatment rates. Recent research has identified some uncertainities associated with soil-bentonite slurry trench cutoff walls due to their potential for construction defects and their long-term performance in terms of waste compatibility and hydraulic fracturing potential (7,8,9). As an alternative, the use of a plastic concrete vertical barrier using the slurry trench method of construction has been described (11) and used on at least one occasion (1).

Plastic concrete is a mixture of cement, bentonite, aggregate and water. A plastic concrete wall is excavated utilizing a panel technique in a manner similar to diaphragm walls. Plastic-concrete is "considerably less stiff at the final set than conventional concrete, although it may be several times stiffer than earth backfill." (16) The use of plastic-concrete cutoff walls may result in the combination of several of the desirable characteristics of both cement-bentonite and soil-bentonite cutoffs.

PURPOSE

An extensive literature review revealed little information regarding the engineering properties, particularly hydraulic conductivity, of plastic concrete, and no information regarding its ability to withstand attack in the hazardous environment. Described in the following sections of this paper are the results of studies conducted to further investigate the engineering properties of plastic concrete as they relate to environmental applications. This paper includes an update of data and interpretations presented earlier (10).

APPROACH

After the assessment of available literature on the topic of plastic concrete, a two-phase laboratory investigation program was designed and implemented. The first phase investigated a wide range of material types and mix proportions. The second phase focused on long-term hydraulic conductivity characteristics including chemical compatibility.

MATERIALS

The materials most commonly used in plastic concrete mixes are cement, bentonite, water and aggregate. (13, 16) In addition to these constituents, both fly ash (type F) and bottom ash were utilized in the laboratory investigations.

Fly ash is the fine residue from the combustion of pulverized coal collected by elecrostatic separators from the flue gases of power plants. Its principal constituents are silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide, (Fe_2O_3), carbon in the form of unburnt fuel, calcium oxide (CaO) and small quantities of magnesium oxide (MgO).

Fly ash is used in concrete as a replacement for cement and is thus an obvious economic advantage. A complete summary of these effects can be found elsewhere (11,12,15).

Bottom ash is also a by-product of coal combustion. It is collected at the bottom of the furnace as inert non-combustible debris. Like fly ash its composition depends on the type of fuel burnt and on the variation of load on the boiler. Bottom ash is comparatively coarse in relation to fly ash. Bottom ash was considered an aggregate substitute.

The cement used was Portland cement type I in accordance with ASTM C150. This is a general purpose cement suitable for all uses when the special properties of other types are not required.

The bentonite utilized met the requirements of the American Petroleum Institute's "Specifications for Oil Well Drilling Materials," API Standard 13A, latest editions, as tested in accordance with the American Petroleum, Institute's "Standard Procedure for Testing Drilling Fluids," API Code RP13B (2).

The water utilized for sample mixing for these studies was tapwater, which complied with the requirements of American Petroleum Institute (2).

Even though aggregates are considered as inert materials acting as filler, they constitute, at times up to 70 percent of the volume of the regular concrete. Aggregates used included a fine aggregate of coarse sand and a coarse aggregate was used having a maximum size of 3/4 inch and meeting the requirements of Grading Size No. 67 of Table 2 of ASTM C33-78 (3).

MIX PROPORTIONING

Several cement-bentonite (CB) mixes were developed as a basis for comparison to plastic concrete mixes. These mixes were used as a check of test procedure to permit comparison of the results with those of other cement-bentonite mixes reported in the literature. The CB mixes also allowed for observation of the effects of fly ash without the additional variable of aggregate. There are six CB mixes, as shown in Table 1, which cover the range of commonly used proportions (14).

Mix proportions for plastic concrete were developed based on proportions of materials in CB mixes and regular concrete mixes. Nine plastic concrete mixes were developed varying aggregate, cement, fly ash, and bottom ash as shown in Table 2.

EQUIPMENT AND PROCEDURES

The hydraulic conductivity of our test specimens was determined utilizing triaxial cell permeameters and generalized procedures described elsewhere (5,16). Additional specimens were fabricated for testing in compaction molds. The data from compaction mold permeability testing were found to be erroneous. The sample shrinkage during curing created space for the permeant to travel around the sample along the walls of the rigid wall permeameter.

It was originally planned to measure shear strength in a triaxial compression test under consolidated-undrained conditions. However, since the strength of plastic concrete exceeded that of the soil testing equipment, it was decided to test only the CB specimens in triaxial compression under consolidated-undrained conditions. The remaining plastic concrete samples were tested in unconfined compression using a Tinius Olsen 10,000 pound testing machine.

RESULTS

WORKABILITY

During the mixing, several observations were made regarding rheologic properties of individual mixes. Increasing amounts of fly ash in cement-bentonite mixes required decreasing amounts of water to maintain the same consistency (slump). The use of the fly ash and bottom ash increases the workability of plastic concrete mixes consistent with the published literature (12).

SHEAR STRENGTH

The results of shear strength tests are summarized in Tables 1 and 2. The two week curing time accounts for a lack of maximum attainable strength. This is particularly true for those mixes with fly ash, where the continuing increase in strength at greater ages is believed to be pozzolanic in nature (12).

In both cement-bentonite and plastic concrete mixes, shear strengths increased with increasing cement content. Fly ash increased strengths of CB mixes where cement content was held constant.

PERMEABILITY

Permeability test results summarized on Tables 1 and 2 were obtained by determining the log average of several hydraulic conductivity determinations for each

Table 1 - Cement-Bentonite

Mix Proportion (by wgt)	Mix No. 1	2	3	4	5	6
Bentonite Content (%)	3.8	3.3	2.8	4.3	3.8	3.3
Water Content (%)	71.3	61.8	52.3	80.8	71.3	61.8
Cement Content (%)	15	15	15	5	15	25
Fly Ash Content (%)	10	20	30	10	10	10
Bentonite/water ratio	0.05	0.05	0.05	0.05	0.05	0.05
Cement/water ratio	0.21	0.24	0.29	0.06	0.21	0.40
Property						
Hydraulic Conductivity ($\times 10^{-6}$ cm/sec)	2.1	1.4	0.9	2.4	3.6	0.5
Shear Strength (kPa)	106	188	358	50	97	573
Axial Strain (%)	0.2	1.1	1.1	0.6	0.9	1.0

Table 2 - Plastic Concrete

Mix Proportion (by weight)	Plastic Concrete Mix No. 1	2	3	4	5	6	7	8	9
Bentonite Content (%)	4.1	4.2	4.1	4.1	4.1	4.1	4.1	4.1	4.0
Fine Aggregate (%)	41.6	41.6	41.6	41.4	41.5	41.3	41.5	41.1	40.4
Coarse Aggregate (%)	33.2	29.1	24.9	29.0	29.1	29.9	29.0	28.8	28.3
Cement Content (%)	4.1	8.3	12.4	6.6	4.1	2.5	6.6	4.1	2.4
Bottom Ash Content (%)	0	0	0	0	0	0	1.7	4.1	2.4
Fly Ash Content (%)	0	0	0	1.7	4.1	5.7	0	0	0
Bentonite/ Water ratio	0.24	0.25	0.24	0.24	0.24	0.24	0.24	0.23	0.21
Cement/ Water ratio	0.24	0.49	0.73	0.38	0.24	0.14	0.39	0.23	0.12
Property									
Hydraulic Conductivity ($\times 10^{-7}$) cm/sec	3.5	1.1	0.5	0.8	1.2	2.0	3.2	18	17
Shear Strength (kPa)	400	338	3427	1455	1214	903	1110	545	76
Axial Strain at failure (%)	2.0	3.7	10.0	5.5	9.8	5.4	12.2	16.8	9.6

sample mix. The coefficient of hydraulic conductivity on the order of 1.0 x 10^{-6} cm/sec for cement-bentonite are within the range reported in the literature (16). The results shown on Table 2 confirm that, depending upon the mix design, plastic concrete can be prepared with coefficients of hydraulic conductivity on the order of 1.0 x 10^{-7} cm/sec or lower.

The hydraulic conductivity generally decreased with increasing cement content. Comparison of fly ash substitution for cement results in higher permeabilities due to the decreasing cement/water ratio in these samples. The hydraulic conductivity was also decreased by utilizing fly ash in addition to cement. In general, plastic concrete mixtures utilizing fly ash display hydraulic conductivities which are an order of magnitude lower than cement-bentonite.

Due to the short curing time of about two weeks, values of hydraulic conductivity in the short term tests did not reach a minimum. Based upon the observed behavior of regular concrete, it is believed that, hydraulic conductivity will decrease with increasing curing time.

To investigate this hypothesis, long-term permeability tests utilizing plastic concrete were initiated. The percentages of various constituents used were those of mix No. 5 (see Table 2). This mixture represents a cost effective substitution of cement with fly ash while maintaining desirable characteristics of high shear strength and low hydraulic conductivity. The permeant utilized was 0.005N calcium sulphate. Typical results of long-term permeation with water are illustrated in Figure 1. There appears to be a slight decrease in hydraulic conductivity with time. This decline in the hydraulic conductivity with time can be attributed to continued hydration of the cement and/or precipitation of calcium sulphate in the high pH environment of the plastic concrete.

COMPATABILITY

Long-term permeability tests utilizing fly ash in plastic concrete were conducted to investigate the compatability to a contaminated pore fluid. Using the same mix as in long-term permeability with water, aniline was introduced into the samples both initially and after initial water permeation. Aniline, an organic base, was used in concentrated form as a permeant. No degradation in hydraulic conductivity due to permeation with concentrated aniline was observed (Fig. 2). In fact, as with the long-term tests with water, continuing decreases in hydraulic conductivity with time are observed. This is in contrast with the significant hydraulic conductivity increases observed when soil-bentonite (7,8,9) or compacted clay (4) were permeated with concentrated aniline.

SUMMARY AND CONCLUSIONS

This study of the use of plastic concrete as an alternative to soil-bentonite or cement-bentonite in slurry trench cutoff walls indicates that plastic concrete may provide an attractive alternate to the conventional technologies for environmental applications. Within the range of parameters tested in these preliminary studies,it was observed that:

1. The hydraulic conductivity of plastic concrete is about an order of magnitude lower than that of cement-bentonite.

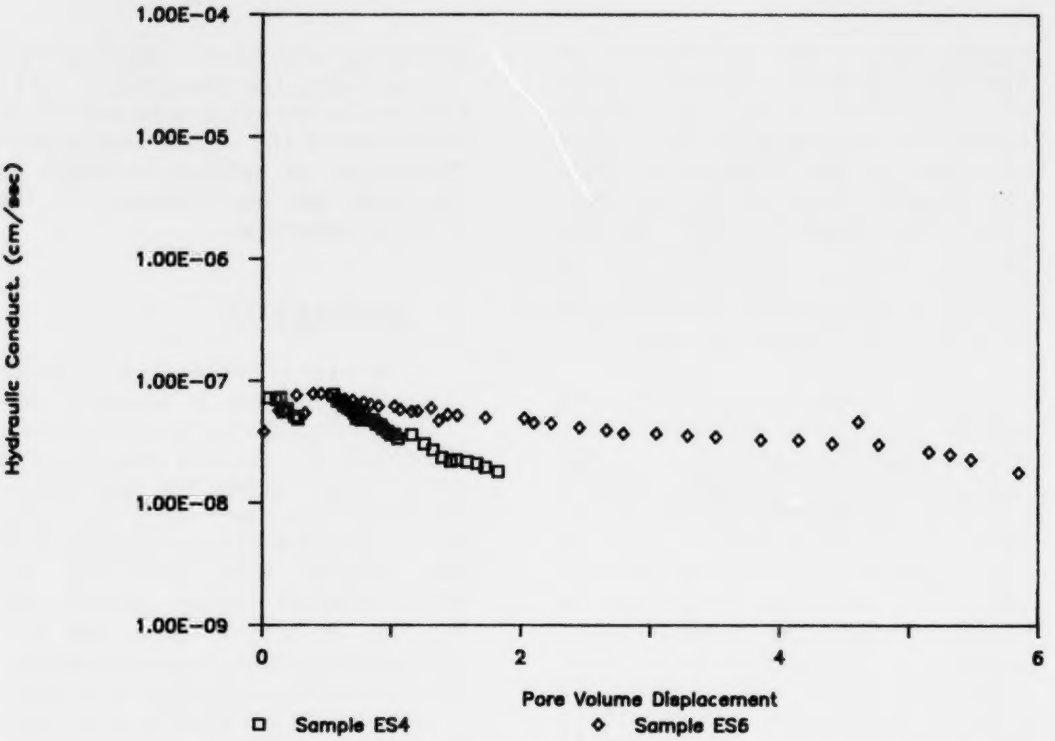


Figure 1 - Permeation with 0.005N Calcium Sulphate

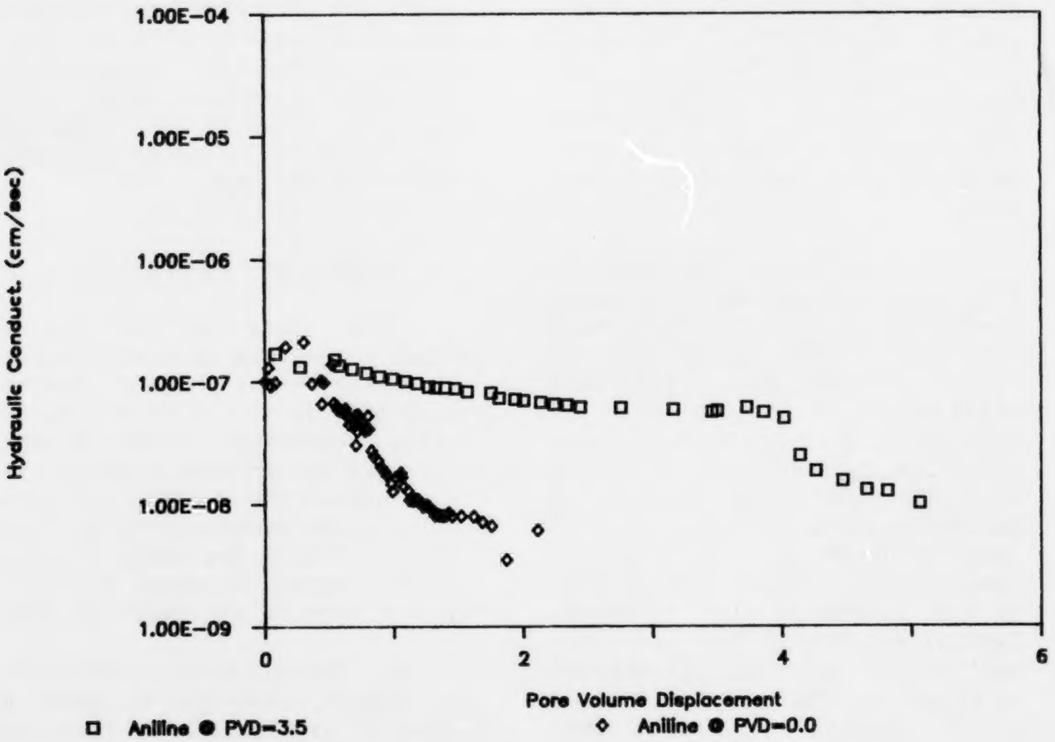


Figure 2 - Permeation of with Concentrated Aniline

2. Increasing cement content generally decreased hydraulic conductivity.

3. Equal replacement of fly ash for cement appears to increase hydraulic conductivity.

4. Increasing cement content increased strength.

5. Hydraulic conductivity decreased with increasing time.

6. Hydraulic conductivity decreased in response to permeation with concentrated aniline.

Plastic concrete would be placed in the excavated slurry trench utilizing the tremie method of concrete placement, offering less potential for construction defects than the conventional method of soil-bentonite backfilling. Further, due to its greater strength, the risks associated with backfill settlement and hydraulic fracturing are decreased. Finally, plastic concrete may offer greater contaminant resistance than cement-bentonite or soil-bentonite. It is therefore concluded that, based on construction, permeability, strength, and compatability considerations, plastic concrete may be an alternative in slurry trench cutoff walls for environmental applications.

It is noted that the variability associated with the properties of fly ash, water, bentonite, and aggregate may influence test results. Additional study is needed for a wider range of materials and contaminants to extend the findings and conclusions reported herein.

ACKNOWLEDGEMENTS

The valuable suggestions provided by the Technical Reviewers is gratefully acknowledged. The authors would like to thank Bucknell University for their financial support of this project. The contents do not reflect the views of the Project Sponsor.

REFERENCES

1. Alaska, W.S. and Cavalli, N.J., "Cement Barriers," Proceedings of the 5th National Conference on the Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., November, 1984, pp. 126-130.

2. American Petroleum Institute, "Recommended Practice for Standard Procedure for Testing Drilling Fluids," Specification RP 13B, 8th Ed., Dallas, April, 1980.

3. American Society for Testing Materials, Annual Book of ASTM Standards, American Society for Testing Materials, Philadelphia, PA 1987.

4. Brown, K. W. & Anderson, D. C., "Effects of Organic Solvents on the Permeability of Clay Soils," EPA-600/2-83-016, 1983.

5. Daniel, D.E., Trautwein, S.J., Boynton, S.S., And Foreman, D.E., "Permeability Testing with Flexible-Wall Permeameters," ASTM, Geotechnical Testing Journal, Vol. 7, No. 3, Sept, 1984, pp. 113-122.

6. Evans, J. C. and Fang, H. Y., "Triaxial Equipment for Permeability Testing with Hazardous and Toxic Permeants," Geotechnical Testing Journal, ASTM,

Volume 9, Number 3, Sept., 1986, 1986, pp. 126-132.

7. Evans, J.C., Fang, H.Y., and Kugelman, I. J., "Organic Fluid Effects on the Permeability of Soil-Bentonite Slurry Walls," Proceedings of the National Conference on Hazardous Wastes and Environmental Emergencies, Cincinnati, OH, May, 1985, pp. 267-271.

8. Evans, J.C., Fang, H.Y., and Kugelman, I.J., "Containment of Hazardous Materials with Soil-Bentonite Slurry Walls," Proceedings of the 6th National Conference on the Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., November, 1985, pp. 249-252.

9. Evans, J.C., Lennon, G.P. and Witmer, K.A., "Analysis of Soil-Bentonite Backfill Placement in Slurry Walls," Proceedings of the 6th National Conference on the Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., November, 1985, pp. 357-361.

10. Evans, J.C., Stahl, E.D., and Droof, E., "Plastic Concrete Cutoff Walls", Proceedings of the ASCE Conference on Geotechnical Aspects of Waste Disposal, Ann Arbor,Michigan, June, 1987, (in review).

11. Haug, M., "Slurry Trench Cutoff", The 1st Canadian Engineering Technology Seminar on the Use of Bentonite for Civil Engineering Applications, Ground Engineering Ltd., Regina, Saskatchewan, March, 1985, pp. 33-52.

12. Helmuth, Richard, Fly Ash in Cement and Concrete, Portland Cement Association, 1987, 203 pp.

13. Orchard, A. F., Concrete Technology, Applied Science Pub., London, England, 1979.

14. Ozomaka, O. J., "Some Shear Strength Parameters of Plastic Concrete," Magazine of Concrete Research, Vol. 23, No. 75-76, June, 1971, pp. 119-126.

15. Troxell, G.E., Harmer, E.D., and Kelly, J.W., Compostion and Properties of Concrete, McGraw-Hill, New York, NY, 1968.

16. Xanthakos, P.P. Slurry Walls, McGraw-Hill, New York, NY 1979.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

STUDY OF TRANSPORT OF CONCENTRATED ORGANICS IN THE UNSATURATED ZONE

Tissa H. Illangasekare
Civil, Environmental, and Architectural Engineering
University of Colorado
Boulder, Colorado 80309-0428

Danny D. Reible
Chemical Engineering
Louisiana State University
Baton Rouge, Louisiana 70803

ABSTRACT

Hazardous waste applied to the soil from spills on the ground surface or as a result of leaks from underground storage facilities are often in the form of concentrated or free-phase organics. While a great deal of progress has been made in the transport and the fate of organic chemicals in dilute aqueous groundwater solutions in recent years, the more complicated and potentially more significant problem of the transport and fate of concentrated organic phase has been largely untouched. After a spill or a leak, estimates on the rate of propagation of the front through the unsaturated zone and the fraction of the chemical which will be entrapped in the soil are of importance in the design of remediation or reclamation schemes in problems of hazardous waste management. The multiphase flow models which are based on traditional approaches adopted from petroleum engineering are mathematically elegant but the data requirements do not permit the use of these models for applications in the field scale which is of interest.

A preliminary set of experiments were conducted in laboratory sand columns with a selected set of organic chemicals with the objective of obtaining a qualitative understanding of the dynamics of the distribution and transport of the different phases. The compounds represent a wide variety of densities and miscibilities. Based on these experiments a simple conceptual model which assumes a piston wetting and drainage front was developed.

INTRODUCTION

As a result of the land application of hazardous wastes, the chemical waste mixture can be transported in soil. Assessment of the ultimate fate of the wastes is dependent upon the physical and chemical properties of the fluid phases and the pore characteristics of the soil. In general, these properties are spatially and temporally inhomogeneous and difficult to estimate and employ in models of the transport and transformation processes. The evaluation of these properties and their incorporation into models are necessary to identify the environmental impact of the land application of the wastes. In addition, remedial action at existing uncontrolled spill, leak and dump sites must be based upon an evaluation of the extent of contamination, which is only possible if qualitative and quantitative understanding of the transport processes is available.

The difficulties associated with accurately assessing the fate of hazardous organic chemicals after land application are exaggerated in the presence of a concentrated or pure chemical phase. Simple methods for estimation of infiltration rates of a free organic in the unsaturated zones are generally unavailable. The effect of such chemicals on the properties of the soil matrix controlling the transport and entrapment behavior is often unknown. Phase interactions, such as mass transfer between phases followed by effects on phase viscosity, interfacial tension and other transport properties, may be significant. while a great deal of progress has been made in recent years on the understanding of the transport and fate of organic chemicals in dilute aqueous ground water solutions the more complicated and potentially more significant problem of the transport and fate of concentrated organic phases has been largely untouched. This is despite the fact that close to the spill the chemical flows as a separate phase and, can remain so for some distance from the source. It is the transport of concentrated organic phases such as these in the air-soil-water matrix that is the subject of this paper.

PURPOSE

Descriptions of transport of hazardous organics in the soil have generally been limited to low concentration, single phase aqueous solutions (e.g. Smiedt and Wierenga, 1984, Ostendorf et al., 1984, and Nielson et al., 1986). Quantitative description of the multiphase mixture flow is generally possible through modified versions of Darcy's law. The pioneering work of Muskat et al. (1937), Buckley and Leverett (1942), Fatt and Dykstra (1951), among others, formulated approaches where Darcy's law was used in conjunction with the concepts of relative permeabilities of different phases. A recent paper by Abriola and Pinder (1985) noted, however, that no single model has been developed with capability of tracing the multiphase migration of a pollutant. the same authors report the development of a one dimensional multiphase flow model to describe the simultaneous transport of organic compounds in a nonaqueous phase, as a soluble component of an aqueous phase, and as a gas phase. This model has been updated to include two-dimensional behavior by Pinder and Abriola (1986). Other numerical models that have been developed to address different aspects of the two phase immiscible flow problem in the near surface environment include those of Faust (1985) and Osborne and Sykes (1986).

In each of the above studies, the distinct phases (water, air and chemical) are assumed to behave as a separate continuum. The treatment of more than one phase requires the introduction of additional parameters resulting from the interfacial tension between the different fluids occupying the pore spaces. Most of the models referred to above assume simple forms for these parameters, neglecting, for example, hysteresis between the various phases.

Despite the simplifying assumptions of these models, their sophistication generally far exceeds that of the available database. At the root of these problems is the difficulty of predicting, or even measuring, the relative permeability as a function of the fluid saturation. The relative permeabilities exhibit significant hysteresis and the verification of the relative permeability models in the presence of three or more phases is still not clear (Stone, 1973; Moline, 1980). Residual saturations, or the field capacities, of each of the fluid phases are also difficult parameters to predict, although they are required in all multiphase flow models. Two phase residual saturations can be measured and correlated with Bond and/or capillary numbers (Wilson and Conrad, 1984; Chatzis et al., 1984) although little data is available in the unsaturated zone to guide the modeler. In three phase flow situations, however, recent work suggests that even the appropriate form of these correlations is not well understood (Abriola and Pinder, 1985).

It therefore appears clear that transport of a concentrated organic phase in the soil due to a spill or leak of hazardous wastes presents technical difficulties that have not been addressed by the classical approaches of ground water hydrologists or petroleum engineers. It also appears that the hydrodynamics of such an organic phase is dependent upon the relative density, viscosity and miscibility of the phase with water. An experimental investigation of these effects has been conducted with the objective of developing both a qualitative and quantitative understanding of the sub-surface transport processes of a concentrated organic phase. The purpose of this paper is to report on the qualitative behavior observed in concentrated phase infiltration in laboratory sand columns and simple sharp front models that were developed based on these observation. This paper will be limited to the transport processes observed in the unsaturated zone due to one-dimensional (vertical) movement of the organic phase.

APPROACH

Experimental Procedure

A fine sand was selected as the porous medium for the initial investigations. Two different sand mixes were employed, one with a mean particle diameter of about 0.3 mm and one with a mean particle diameter of about 0.4 mm. The chemicals employed for the experiment were selected to exhibit a range of densities and miscibilities with water. The chemicals used, and their physical properties are listed in Table 1. Several experiments were conducted to determine the suitability of various column construction materials for each chemical. For all but the chlorinated organics, it was found that a plexiglass column was sufficient. To provide the most flexibility with the experiments and the organic selection, however, a glass column was also fabricated. Both column were approximately 6.35 cm ID and about 150 cm long.

The general problem of the movement of an immiscible fluid in unsaturated soils requires the consideration of all the possible soil water content profiles in the aquifer zone between the water table and the ground surface. Perhaps the most common physical situation is one where the upper layers of soil are initially drained to field capacity (residual water saturation). The preliminary laboratory experiments were focused on chemical infiltration under these condition. After draining the water to residual saturation the appropriate chemical phase was introduced to the soil surface,

Table 1. Physical Properties of Candidate Compounds

Compound	ρ	S mg/L	P_v mm Hg	ν cSt	σ_s	σ_i dyne/cm
water	1.00	-	17.5	1	73	-
Immiscible Organics (S < 1 g/L)						
Carbon Tetrachloride	1.59	800	89.6	0.61	26.8	
1-octanol	0.82	300	<1	12.2	27.5	8.5
Transmission Oil-A	0.87	<1		20		
Miscible Organics (S > 1 g/L)						
Chloroform	1.48	8200	159.6	0.38	27.1	45.0
Methanol	0.79	-	127.2	0.69	22.6	

All properties at approximately 20°C

ρ = Specific gravity relative to water; S = Water solubility; P_v = Vapor Pressure; ν = Viscosity; σ_s = Surface tension with air; σ_i = Interfacial tension with water

typically at constant ponded depth for some time followed by a no-addition infiltration period. Visual observations during infiltration experiments with immiscible organic phases, such as the automatic transmission fluid quickly indicated that the organic wetting front was distinctly sharp and horizontal. Dyes in the water phase also indicated that there was little or no movement of the residual water due to the passage of the immiscible organic phase. After complete infiltration of the ponded organic at the top of the column, a "drainage front" appeared that was initially diffusive but sharpened as the organic phase continued to drain.

Simple Sharp-front Model

As the organic moves through the soil pores, a front will develop as a result of the organic saturating the pores which were originally partially filled with water. This front is truly diffusive as the chemical entering the soil pores will not instantaneously saturate them. In conceptualizing the simple model proposed here for the immiscible organics the assumption of a sharp advancing front is made. Behind this front the soil pores are assumed fully saturated with the immiscible organic and the residual water. A very small amount of air may be entrapped within the soil pores. These air pockets are not interconnected and could be assumed immobile thus avoiding the need to consider the air as a third phase in this simplified multiphase flow problem.

Assuming complete immobility of the residual water, the governing equation for the organic phase can be written by combining Darcy's law and continuity equation. This is of the form:

$$\frac{\partial \theta_f}{\partial t} + \frac{\rho_f g}{\mu_f} \frac{\partial}{\partial z} \left[k(\theta_f) \left(\frac{\partial h_f}{\partial z} - 1\right)\right] = 0 \qquad (1)$$

where θ_f is the volumetric organic content in the soil, ρ_f and μ_f are the density and dynamic viscosity respectively, of the organic, z is the vertical coordinate defined positive downward, and $k(\theta_f)$ is the permeability of the organic phase.

Under ponded conditions on the soil surface the distribution of the volumetric organic content as a function of depth is shown on Figure 1. In this figure, θ_{wr} is the residual water content which is assumed to be uniform along the z axis, $\tilde{\theta}_{wf}$ is the total volumetric phase content of water and the organic when the pores are under natural saturation, and ϕ is the porosity of the soil.

The partial volumetric phase content of the organic at natural saturation is given by:

$$\tilde{\theta}_f = \tilde{\theta}_{wf} - \theta_{wr} \qquad (2)$$

In the proposed simple model it is assumed that the wetting front formed by the moving organic phase is sharp. As the volumetric phase content of the organic fluid is constant behind the front,

$$\theta_f = \tilde{\theta}_f \text{ and } \frac{\partial \theta_f}{\partial t} = 0 \text{ for } 0 \leq z \leq z_f \qquad (3)$$

Also, with the assumption of immobility of the residual water phase, the permeability $k(\tilde{\theta}_f)$ remains constant behind the front.

Incorporating all of the above conditions in Eq. 1, one obtains:

$$\frac{\partial h_f}{\partial z} = \text{constant for } 0 \leq z \leq z_f \qquad (4)$$

The Darcy flow velocity of the organic phase is given by:

$$v_f = -\frac{k(\tilde{\theta}_f)}{\mu_f} \rho_f g \frac{\partial h}{\partial z} \qquad (5)$$

where h is the total head ($h = h_f - z$). As $\frac{\partial h_f}{\partial z}$ is constant behind the front the total head gradient $\frac{\partial h}{\partial z}$ remains constant. By selecting two points at the leading edge of the front and at the ground surface, respectively, the constant head gradient behind the front could be expressed as,

$$\frac{\partial h}{\partial z} = \frac{1}{z_f} [h(z_f) - h(o)] \qquad (6)$$

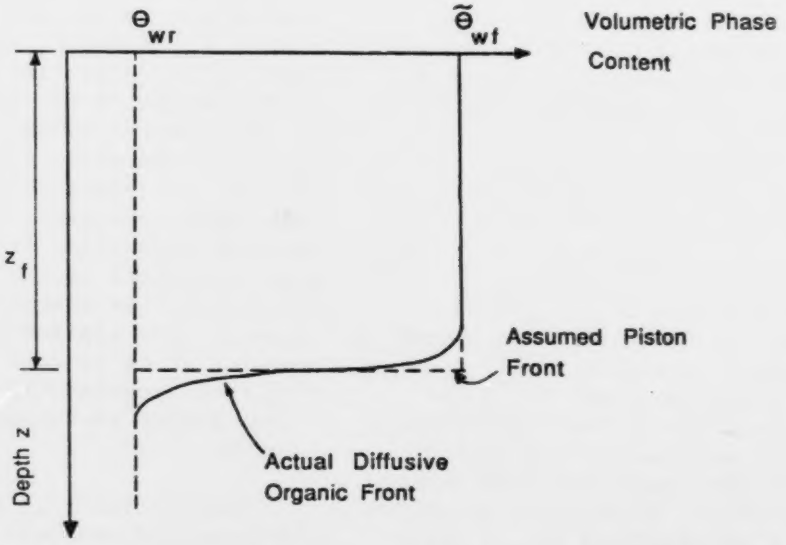


Figure 1: Distribution of Volumetric Phase Contents Under Ponded Conditions on the Ground

where $h(z_f)$ and $h(o)$ are the total head in the organic phase at the front and the ground surface, respectively. The total head at the ground surface is the sum of atmospheric pressure head h_A and the ponded depth, $H(t)$ of organic above the ground surface. That is,

$$h(o) = h_A + H(t) \tag{7}$$

Defining H_f as the capillary suction head at the front, the total head at the front is given by,

$$h(z_f) = h_A - H_f - z_f \tag{8}$$

Substituting Eqs. (6), (7) and (8) in Eq. (5), the Darcy velocity of the organic phase is obtained as

$$v_f = \frac{k(\bar{\theta}_f)\rho_f g}{\mu_f}\left[\frac{z_f + H + H_f}{z_f}\right] \tag{9}$$

This velocity can also be written as

$$v_f = \bar{\theta}_f \frac{dz_f}{dt} \tag{10}$$

Equations 9 and 10 can be combined to obtain the differential equation relating the time of observation to the position of the chemical front. This equation is given as

$$\bar{\theta}_f \frac{dz_f}{dt} = \frac{k(\bar{\theta}_f)}{\mu_f} \rho_f g \left[1 + (H + H_f)\frac{1}{z_f}\right] \tag{11}$$

Equation (11) can be integrated subjected to the appropriate initial and boundary conditions.

In these equations $k(\bar{\theta}_f)$ is the permeability of the organic fluid at natural saturation. Since the available pore space has been reduced by the presence of residual water and air, this permeability is, in general, different from the saturated permeability if the fluid alone is flowing through the soil.

The capillary suction head term H_f, lumps all the capillary suction effects at the diffusive front. Morel-Seytoux and Khanji (1975) defined a term "effective capillary drive" to approximate the capillary suction. This could either be treated as an empirical coefficient to be determined experimentally, or could be related to the mechanical properties of the medium and the physical properties of the organic fluid.

The expected phase distribution profile after the ponded depth goes to zero and during the subsequent drainage is shown on Figure 2. The position of the assumed drainage front is defined at a depth z_b from the ground surface. Behind the drainage front it is assumed that the organic fluid is at a constant residual saturation θ_{fr}.

Immediately after the ponded depth goes to zero, the zone between the two fronts remains at natural saturation $\bar{\theta}_{wf}$. The depth of this zone of saturation will decrease with time. If the initial wetting front depth z_f is large this zone will remain saturated for a longer time. As quantitative measurements to determine the phase content profiles were not performed in these initial experiments the exact time of occurrence of transition from the saturated conditions to drainage was not determined. As adequate depths of organics were applied on the soil surface, it is assumed that the wetting front reached the bottom of the column before the transition started.

The gradients of the head within the saturated zone can be obtained by considering the head drop between the drainage and the wetting fronts at depths z_b and z_f, respectively.

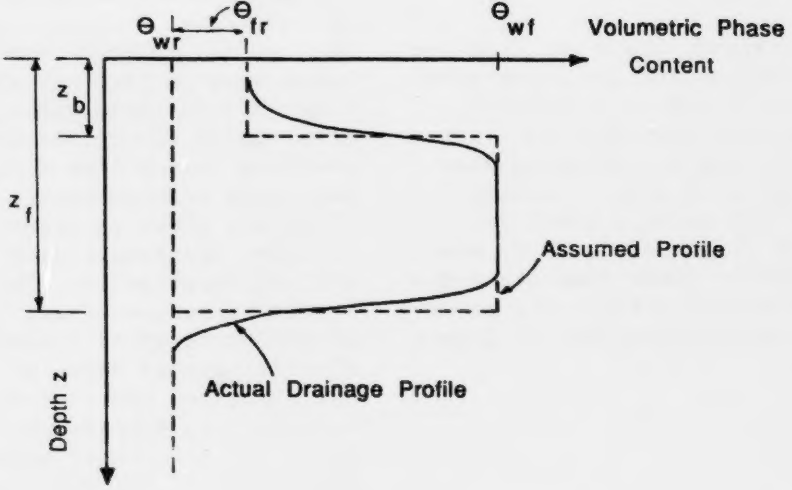


Figure 2: Distribution of Volumetric Phase Contents Under Drainage with no Surface Ponding

The constant head gradient for the linear head distribution within the saturated zone is given by

$$\frac{\partial h}{\partial z} = \frac{H_b - H_f - (z_f - z_b)}{z_f - z_b} \qquad (12)$$

Applying Darcy's law, the velocity within the saturated zone is,

$$v_f = -\frac{k(\tilde{\theta}_f)\rho_f g}{\mu_f}\left[\frac{H_b - H_f - (z_f - z_b)}{z_f - z_b}\right] \qquad (13)$$

The velocity can also be written in terms of the rate of propagation of the wetting front as was given by Eq. 10. Because of the additional variable z_b which was introduced for this drainage case, a third equation has to be introduced. At any time during drainage, the total depth of organic fluid within the profile is equal to the total spill depth. Defining the cumulative application (or spill) depth as W(o) the following relationship is obtained by considering the conservation of volume:

$$z_f\tilde{\theta}_f - z_b(\tilde{\theta}_f - \theta_{fr}) = W(o) \qquad (14)$$

Combining Eqs. 10, 13 and 14 to eliminate v_f and z_b, the following differential equation for the unknown front depth z_f is obtained.

$$\theta_f \frac{dz_f}{dt} = \frac{k(\tilde{\theta}_f)\rho_f g}{\mu_f}\left[1 + (H_f - H_b)\frac{(\tilde{\theta}_f - \theta_{fr})}{W(o) - z_f\theta_{fr}}\right] \qquad (15)$$

This governing equation can be integrated for appropriate initial and boundary conditions. Computer programs to simulate the front position z_f as a function of time for the two situations of front propagation and drainage were developed.

PROBLEMS ENCOUNTERED

The drainage front was less defined in the qualitative experiments due to the difficulty in observing the contrast between the color intensity in the organic saturated zone and the entrapped zone. Ongoing investigations using a gamma ray attenuation system designed to measure volumetric phase contents and a pressure scanning system will generate more quantitative data to locate the fronts.

RESULTS

The developed program allows specification of a constant head period of arbitrary length followed by falling head and drainage periods. Parameters (effective conductivity, effective capillary suctions at leading and trailing edges of front) were estimated directly from the experiments using an optimization method (Powell's Method of Conjugate Directions) to produce a non-linear least squares fit between model and experiments. Comparison of the model predictions of organic wetting front position versus time during three experiments with automatic transmission fluid are shown in Figure 3. One set of model parameters were used to fit all oil experiments. The differences between experiments are the results of different initial conditions (initial ponded depth of organic and its duration) and sand types. The extremely good agreement between model and experiment belie the simplicity of the model and provide little justification for more elaborate modeling efforts for this particular case.

Table 2 summarizes the best fit effective fluid permeabilities. Note that the effective fluid permeability in the final column is essentially

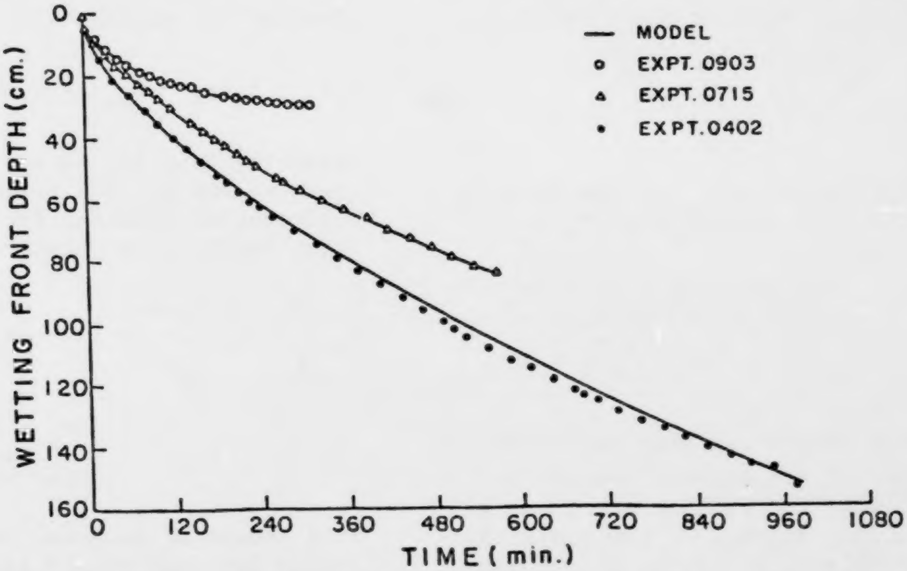


Figure 3: Comparison of Sharp Front Model with Experimental Results of Automatic Transmission Oil

Table 2. Infiltrating Liquid Permeabilities.

Date	Compound	K cm/min	ν cSt	k intrinsic cm^2 x 10^9
Sand 1 - d = 0.3 mm				
7/17	Carbon Tetrachloride	1.17	0.61	120
4/2	Transmission Oil-A	0.035	20.	118
4/8	Transmission Oil-A	0.033	20.	114
5/8	Transmission Oil-A	0.028	20.	96
6/13	Transmission Oil-A	0.024	20.	82
7/9	Transmission Oil-A	0.029	20.	99
7/15	Transmission Oil-A	0.037	20.	127
			Average	108
Sand 2 - d = 0.4 mm				
9/5	Carbon Tetrachloride	1.86	0.61	192
9/8	Carbon Tetrachloride	2.46	0.61	253
9/6	Methanol	2.41	0.69	281
9/9	Methanol	1.78	0.69	208
8/28	Transmission Oil-A	0.067	20.	229
9/3	Transmission Oil-A	0.078	20.	264
			Average	238

constant. Under the conditions of the study, the effective intrinsic permeability was also observed to be nearly identical with the saturated intrinsic permeability.

Table 3: A Summary of Preliminary Results on Calibrated Capillary Suction Heads.

Compound	Sand Type	Average H_f (cm)	Average H_f (cm)
Water	1	51.8	46.6
	2	16.5	14.4
Transmission Oil-A	1	12.4	10.4
	2	-2.6	10.4
Carbon Tetrachloride	1	28.1	35.0
	2	-1.4	15.5
Chloroform	1	-4.4	30.1
	2	-14.3	29.4
Methanol	2	45.5	28.8

Table 3 summarizes the calibrated values of the two suction heads using the model. In this case the intrinsic permeability of each sand was provided to the model and the suction head values were optimized to obtain the best fit for the experimental data.

Using the calibrated parameters the model was used to predict the propagation of wetting fronts. Sample results for two of the chemicals are shown in Figures 3 and 4.

Preliminary experiments conducted in vertical sand columns at residual water saturation indicated that simple sharp front models can describe the basic transport behavior of such phases under those conditions.

The results of the preliminary investigations with the miscible organics showed that the same simple model could adequately describe the transport by using the same effective

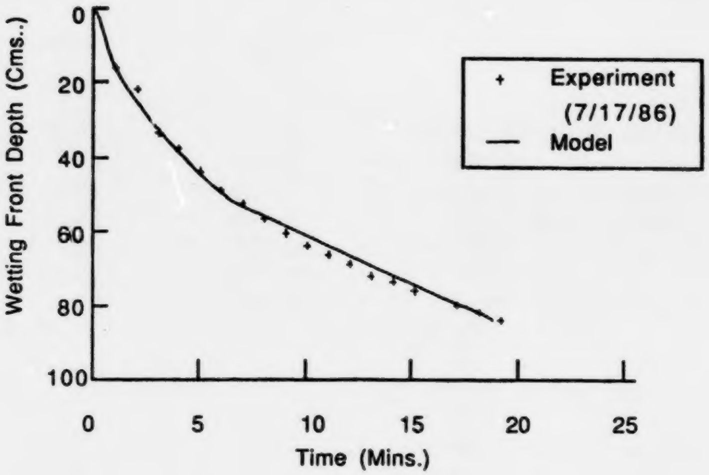


Figure 4: Comparison of Sharp Front Model with Experimental Results for Immicible Organic - Carbon Tetrachloride

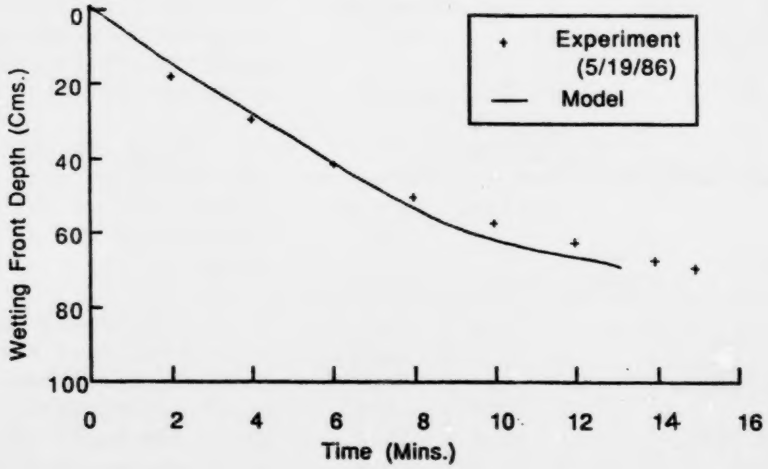


Figure 5: Comparison of Sharp Front Model with Experimental Results for Miscible Organic - Chloroform

intrinsic permeability. The results of these investigations were not discussed in this paper. It was observed that the region of dissolution for miscible organics was limited to a thin zone and thus most of the miscible organic was contained within an essentially pure phase. The simple sharp-front model developed for the immiscible fluids can be adopted for the miscible fluids by incorporating a front dispersion model for the dissolution zone. The model development efforts for this application is currently in progress.

These extremely simple models of the one-dimensional infiltration of organic phases represent preliminary efforts towards understanding and describing the more general problem. More general situations associated with real soils and soil-water distribution profiles have to be investigated. Despite the preliminary nature of the work, however, the results are encouraging and the developed models appear useful for crude exposure assessment type estimates of free phase organic transport.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support received from the U.S. Environmental Protection Agency, Hazardous Waste Research Center at Louisiana State University and the National Science Foundation (Grant CEE - 8405881). Also, we would like to express our appreciation and gratitude to Dr. Louis J. Thibodeoux for his constant encouragement, support, and sharing his thoughts on the subject area discussed in this paper.

REFERENCES

1. Abriola, L. and G.F. Pinder (1985) A multiphase approach to the modeling of porous media contamination by organic compounds 1. Equation development. Water Resources Research, 21 (1) 11-18.

2. Buckley, S.E. and M.C. Leverett, Mechanics of fluid displacement in sands. Transactions, American Institute of Mining, Metallurgical, and Petroleum Engineers, 146, 107-116.

3. Chatzis, I. and N.R. Morrow (1981) Correlation of capillary number relationships for sandstones. Society of Petroleum Engineers, paper # 10114.

4. Chatzis, I., M.S. Kuntamukkula and N.R. Morrow (1984) Blob size distribution as a function of capillary number in sandstones. Presented at the 59th Annual Technical conference of the Society of Petroleum Engineers, Houston, Texas, Sept. 1984.

5. Fatt, I., and H. Dykstra (1951) Relative permeability studies. Transactions, American Institute of Mining, Metallurgical, and Petroleum Engineers, 192, 249-256.

6. Faust, C.R. (1985) Transport of immiscible fluids within and below the unsaturated zone: A numerical model. Water Resources Research, 21, (4) 587-596.

7. Green, W.H. and G.A. Ampt (1911) Studies on soil physics: I. Flow of air and water through soils. Journal of Agricultural Research, 4 1-24.

8. Molina, N.M. (1980) A systematic approach to the relative permeability problem in reservoir simulation, Presented at the Annual Fall Technical Exhibition of the Society of Petroleum Engineers.

9. Morel-Seytoux, H.J. and J. Khanji, (1975) Equation of infiltration with compression and counterflow effects, Bull. Internat. Assoc. Sci. 20(4) 505-517.

10. Muskat, M., R.D. Wykoff, H.G. Botset, and M.W. Meres (1937) Flow of gas-liquid mixtures through sands. Transactions, American Institute of Mining, Metallurgical, and Petroleum Engineers, 123, 69-96.

11. Nielson, D.R., M.Th. van Genuchten and J.W. Biggar (1986) Water flow and solute transport processes in the unsaturated zone, Water Resources Research, 22 (9) Supplement, 89S-108S.

12. Ng, K.M., H.T. Davis and L.E. Scriven (1978) Visualization of blob mechanics in flow through porous media. Chemical Engineering Science, 33, 1009-1017.

13. Osborne, M. and J. Sykes (1986) Numerical modeling of immiscible organic transport at the Hyde Park landfill, Water Resources Research, 22 (1), 25-33.

14. Ostendorf, D.W., R.N. Noss and D.O. Lederer (1984) Landfill leachate migration through shallow unconfined aquifers. Water Resources Research, 20, 291-296.

15. Pinder, G.F. and L.M. Abriola (1986) on the simulation of nonaqueous phase organic compounds in the subsurface. Water Resources Research, 22 (9) (Supplement), 109S - 119S.

16. Smiedt, F. De and P.J. Wierenga (1984) Solute transfer through column of glass beads. Water Resources Research, 20, 225-232.

17. Stone, H.L. (1973) Estimation of the three-phase relative permeability and residual oil data, J. of Canadian Pety. Tech. 12, 53-61, Environmental Research Laboratory, Athens, GA 30613.

18. Wilson, J.L. and S.H. Conrad (1984) Is physical displacement of residual hydrocarbons a realistic possibility in aquifer restoration? In Petroleum Hydrocarbons and Organic Chemicals in Ground Water, National Water Well Association, Washington, OH 43085.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

WORLDWIDE PERSPECTIVE ON THE DISPOSAL OF SOLID WASTES FROM MINING OPERATIONS

Jacek S. Libicki
POLTEGOR
Powstancow SI.95, 53-332 Wroclaw, Poland

ABSTRACT

Mining operations and minerals treatment produce about 15-20 billion tons of solid wastes per year. The area occupied each year for disposal reaches about 500 km2. Although the solid wastes from mining (besides radioactive ones) are less hazardous to the environment than many other industrial wastes (mostly due to relatively small concentration of pollutants) their great volumes have a substantial impact on almost all components of the environment. This impact is manifested in change of original land use, and the pollution of soils, groundwater, surface water and air as well. In various countries, very different laws and regulations, from very stringent to relatively liberal, are in force for the disposal of mining wastes. In many countries there are practically no laws or regulations in force in regard to those procedures. Whether the efforts in research and practical implementation are concentrated on waste utilization and/or on environmentally accepted disposal operations depends on the kind and volume of wastes, legal status and land management policy in the country, or the part of the country, where the mining wastes are produced. However, in very many countries no research has been conducted until now. Examples of research from some countries, in different areas of the world, with various economical systems and degrees of development, are discussed in this paper. Those countries are Australia, Canada, China, Federal Republic of Germany, Poland, United Kingdom, Union of Soviet Socialist Republic and some others.

INTRODUCTION

The disposal of solid wastes resulting from mining and mineral treatment has always had a deteriorating impact on many environmental components. One disturbed environmental component is land originally used as farmland, forest, pasture or for wildlife refuges. Very often the landscape is changed by forming artificial elevations or by filling in valleys. Sometimes disposals sites filled to a high elevation can be dangerous for the vicinity because of the potential landslide hazard. Another threatened environmental component is water, both groundwater and surface water (rivers, lakes and even seas). Surface waters are disposed directly to the sea or lake, or indirectly, when rainwater percolates through the disposal site, leaches pollutants from the material and then flows to the stream or lake. Groundwater pollution can also be direct or indirect. Direct pollution occurs when the wastes are placed within the aquifer and have immediate contact with groundwater. Indirect pollution occurs, when the disposal site is located over the aquifer. In this case rainwater leaches the pollutants and percolates to the aquifer, so the aquifer is recharged with polluted water. Air pollution can be effected by dust emission and wind transportation of fine particles. Also the effect of spontaneous combustion of coal wastes can cause gas and smoke to spread around the disposal area. Soils around the disposal areas can be polluted through air or water propagation of pollutants. The volume of solid mining wastes produced all over the world is estimated to be about 15 to 20 billion tons per year and the area occupied for disposal areas is about 500 km2. Therefore, solid wastes from mining, because of the large volumes, can cause important effects on the environment; i.e., in the close vicinity of operations (land use and air pollution), within a radius of several miles (groundwater) and at even longer distances (surface water of downstream rivers).

Various countries treat this matter with varying degrees of concern and give it various priorities. There are also different laws and regulations for environmental protection.

PURPOSE

The purpose of the paper is to give a global review of the research, industrial practices and the legal status of solid waste disposal in the mining industry. In order to limit the size of the paper, selected countries will be used as examples and from those countries some typical issues are presented. Another aim is to allow the reader the opportunity to make comparisons with his own native experience. Also the paper presents information regarding advanced research in particular countries and the anticipated future of mining waste disposals.

APPROACH

Legal Status

Three groups of countries can be distinguished based on legislation related to solid mining wastes disposal:
GROUP I- countries where mining wastes disposal is subordinate to mining, environmental or land management laws and

regulations. This group can be subdivided into two subgroups: Subgroup IA of countries where all regulations are executed with full consistency; and

Subgroup IB of countries where regulations exist but their execution is sometimes not applied because industrial lobbies are stronger than environmental ones and various arguments can often obtain relief, e.g., unemployment, lack of foreign currency for importation, etc. To Group I belong such countries as the U.S.A., U.K., Fed. Rep. of Germany, Poland and the U.S.S.R. The classification into subgroups is here more difficult and delicate as regulations differ even within particular countries. GROUP II- countries where some mining and environmental regulations exist, but their application to mining waste disposal is so vague the possibility exists for their arbitrary interpretation. In these countries, the mining companies can quite easily omit the regulations and obtain the permit for wastes disposal without special limitations. Spain, Yugoslavia, Greece, Turkey, some provinces of Canada and Australia (Tasmania), as well as a few more advanced Third World countries belong to this group.

GROUP III- countries where special mining waste disposal regulations do not exist and thus disposal sites can be effected in the most convenient place selected by the mining company. Practically all Third World countries such as China, Zambia, Chile, Columbia, Papua-New Guinea, Malaysia and others. It should be mentioned here that in many countries, especially those of federal structure the regulations concerning waste storage are left to local (state, provincial, regional) authorities. So, for example, they vary between individual provinces of Canada or states of Australia. In some countries where regulations are similar, their differ in particular areas of the country. An example is Poland where permit requirements for mining waste disposal, and the execution thereof, are always under the local authorities. However, in the U.S.S.R., the local authority must have approval of the Federal Ministry of Geology for minerals of nationwide importance. In many countries belonging to these groups, the problem exists of wastes disposal operation conducted before regulations came into effect. Regulations relating to disposal planning, construction and pollution control came into effect only within the last 10 to to 15 years. These older disposal sites are usually treated more liberally than new ones and mining companies try to extend their use as long as possible. Examples here are Poland, Canada and many other countries.

Australia

Solid mining wastes in Australia originate primarily from coal mining (salted overburden and coal accompanying strata) and from uranium mining. The regulations related to waste disposal are issued by each state. In all states, permits are required and Australia's first regulations were enacted during the early 1970's. States have various approaches to these operations and different requirements. The most detailed regulations relate to surface water. For instance, in Victoria the polluted water leaking from the disposal site to the stream cannot increase the stream's TDS content by more than 500 ppm, whereas in the Northern Territory, TDS cannot be changed at all. The catchement areas are divided into three groups-unrestricted, restricted and non-released. Waste disposal permits are commonly issued for 15 years with right of extension. If new requirements come into force during the disposal operation the company receives an allotted time for adjustment. Groundwater protection requires that there be no changes in its original quality. Permit applications must present geological structures, original groundwater quality, stratigraphic relations of aquifers, leachability of soils and salinity release. Very often cutoff walls, superficial sealing, or closed circulation of polluted water is required. For land protection, disposal sites are reclaimed in ways satisfactory to the local authorities. Reclamation relates to both landscape shaping and revegetation effected progressively in a reasonable time. The period of allotted time for reclamation is not strictly codified in the regulations but must be approved by the local authorities. Type of reclamation (arable land, pasture, forest) is adopted by the mining company which runs the farm or ranch atop the reclaimed area. Depending on the project size, the State Minister of Environment decides whether a full Environmental Impact Study is required or a Preliminary Environmental Report is sufficient. Public hearings are a common procedure before decisions are finalized. The practical execution of regulations differs in particular states with the most stringent being Victoria and the Northern Territory, while more liberal areas include South Wales, Queensland, and South and West Australia (except water protection). Tasmania remains the most liberal because of its interest in attracting new investments. Research projects are financed from Federal and State funds, as well as from private sources. A Federal Agency called Commonwealth Scientific and Industrial Research Organization conducts basic and applied research and the reports are commercially available. A private company, AMARA, specializing in mining research, operates on private contracts. The universities do not perform research in this field. Priority mining waste disposal research have in sequence: salinization of water and soils, conservation of water (don't use water more than necessary) and land protection in the Northern Territory where special care is being taken to protect the native style of life and the semiaridness of the natural environment.

Canada

Canada is a country where the mining and mineral industries comprise a large portion of the national economy. However, due to the size of the country and the small population density the mining industry is more uniformly dispersed than in Europe. With few exceptions (asbestos in Quebec) there are no specific areas where high concentrations of mining waste disposals could be burdensome to densely populated environs. Canada, like Australia, is a Federal Country and as such, its provinces possess a great amount of independence in mining and environmental legislation. South of the parallel 60', mineral resources and environmental protection, including mining wastes disposal, is in the hands of provincial authorities. North of the parallel 60', these responsibilities are in the hands of the Federal government. The exception being uranium mining and radioactive waste disposal which remain under the Federal Government's dicta throughout Canada. Because most of Canada's mining occurs south of the parallel 60', provincial regulations and their enforcement are predominant. However, the Federal Government retains supervisory control of Canadian inland waters but it has executive authority to pass that right to the Provinces. The following laws governing mining wastes disposal have been passed at the Federal level:
Fishery Act- a water protection law which covers mining since 1977; provincial regulations must be more stringent than this law;
Clean Air Act- a rather general Act because federal rights are limited in this domain; detailed requirements relate only to asbestos wastes;
Ocean Dumping Control Act- an Act which regulates waste dumping, with the exception of mining wastes; Northern Inland Waters Act- an Act which applies especially stringent requirements to the Northern Territories; and, the Environmental Contamination Act.

Assessment of the potential hazard of wastes is done in accordance with U.S.EPA standards, but the disposal practices are generally more liberal than in the USA. For example, since 1960 in Northern Quebec the iron ore treatment wastes from a mine producing 40 million tons per year have been dumped in a particular lake. Such a permit probably would not be issued presently, although the water pollution in the lake is less than would be expected. In the same province (70 miles south of Quebec City) exists the largest asbestos mining basin in the world. Mining wastes disposal sites (serpentine and containing asbestos) 50 meters high, with little reclamation or dusting protection, are located within close vicinity of towns of several thousand inhabitants. The first attempts toward reclamation have only just begun. In British Columbia, the AMAX Co., runs a molybdenum mine and received a permit to dump wastes directly to the ocean. On the northern cap of Vancouver Island at Port Hardy, the Island Copper Mine (Utah Mine Ltd.) dumps to the bay of Pacific Ocean 100,000 tons per day of copper treatment wastes with the distance of wastes discharge to the open ocean being 30 kms. The permit for disposal was preceded with tests showing Mo and Cu ions concentration passing to the ocean water at low rates but tests for other heavy metals probably were not conducted. Within the bay, water is sampled at 5 monitoring stations twice a year from depths of 0.5 m, 30 m and 75-135 m depending on the bay depth. Heavy metals such as Cu, Mo, Mn, Zn, As and Hg are designated for testing. The results show an increase of 20 to 50 percent in these metals compared to the original water. Fishes and other water animals and plants did not contain a significant increase of heavy metals.

Research programs concerned with the influences of coal mining wastes disposals on the water environment are conducted by the Federal Environmental Protection Service in Ottawa. High contents of Al (up to 42,000 ppm), Fe (up to 37,000 ppm), Cd (up to 0.9 ppm) and Hg (up to 0.13 ppm) have been found. The Geological Survey conducts research projects looking for best locations for radioactive wastes disposal sites within the Canadian Shield. On a macroscale, satellite remote sensing techniques are used to locate the lineaments which could act as a specialized route for pollutant migration. On a microscale, aerial measuring of the magnetic field gradient (with two monitors hanging vertically one meter below the airplane) gives excellent results. Very extensive and advanced research is conducted at the University of Waterloo (Ontario) and the University of British Columbia at Vancouver to discern the influence of waste disposal sites on groundwater and on pollutants migration in groundwater.

China

The volume of mining wastes produced in China is about one billion tons per year and 75 percent is coal mining wastes. Until recently there had been no environmental regulations related to mining wastes storage. The current practice in flat areas is a cone shaped heap and in the hilly areas, slope dumping or valley filling. The main sources of environmental pollution are dusting, smoke and gasses from spontaneous combustion and the leaching of pollutants to streams. Groundwater pollution presently remains undiscussed. In an attempt to reduce environmental destruction, research has begun to implement the utilization of wastes, e.g., bricks, cement, construction; however, these are only first attempts and the problem remains far from being solved. Mining wastes disposals practices are still based only on technical and economical criteria.

Federal Republic of Germany

In the Fed. Rep. of Germany, the major mining wastes are coal wastes. At a production rate of some 85 million tons of coal per year, the volume of wastes is about 75 to 80 million tons. The present-day and future waste management is as follows (1,2):

Management		1980's	1990's
Construction	%	25-28	25-27
Backfilling	%	7-9	17-23
Disposals	%	68-64	58-50

Some 80 percent of all coal mining wastes, some 65 million tons, is produced in the Ruhr Coal Basin where 5.4 million people live on an area of 4,432 km2. These coal wastes disposal sites currently occupy an area of 0.6-1.0 km2 per year where statistics show 900-1200 people could live, and will, by the year 2000, cover 10-15 km2, an area needed for about 15,000 people. Large-scale problems of land management are imaginable taking into account that approximately 200 spoil heaps presently cover an area of some 30 km2. The coal mining waste management and disposal in the Ruhr Coal Basin is supervised by Kommunalverband Ruhrgebiet (KVR), an association of municipalities. The KVR approach is that no coal wastes are dumped on piles if it is possible to utilize them. So, main efforts have been undertaken in this region to reduce disposal areas by extending coal waste utilization and thereby avoiding negative environmental effects. The research efforts have been concentrating on two areas of coal waste utilization. One involves the increased use of non-treated wastes for earthworks, with 6.5 million tons per year currently being used for road and railway embankments, and for hydrotechnical constructions, with 5.5 million tons per year incorporated into dams and dikes. The use of coal wastes for these purposes is carefully studied to assess the impact of these constructions on the environment. A new idea has been to treat the coal wastes by mechanical and thermal methods in order to obtain light concrete fillers that might replace natural gravel or to produce bricks in combination with lime. Different alternatives using burnt and non-burnt coal waste materials with admixtures of binding components are examined at the pilot building sites and road construction sections. The aim is to evaluate their resistance against strong long-time stresses; however, the implementation of these materials into actual use is slow. A method of aluminum recovery from coal wastes has been developed on a laboratory scale, but the economics of the process are poor at present day prices. Environmental assessments of these studies are focused on the influences of spoil heaps on climate, on air pollution, on soils development on spoils, on natural plant succession, on quick covering with greenery, on the natural settlement of animals on spoil tips and its ecological significance and on extension of usage of reclaimed terrains.

Poland

In Poland, as in Germany, the solid mining wastes come primarily from coal mining (3). The issue of wastes disposal faces important challenges because 50 million m3 (about 100 million tons/year) of coal wastes is produced within an area of 650 km2, the Silesian Coal Basin. This is a production rate of 150,000 tons of coal per year per one km2 of area with a population density of 580 people. Eventually the capacity of old coal wastes disposal sites located in the vicinity of mines will be exhausted with the consequent need for new disposal sites. Environmental requirements for the new mining wastes disposal sites will be stricter than ones currently in effect for the older waste sites. Currently, the Water Law, Mining Law, Environmental Protection Law, Farmland Protection Law, and numerous detail regulations issued in the 1970's and 80's are in force. A site study for mining wastes disposal sites must comprise a complete evaluation of its effect on all elements of the environment, i.e., land withdrawal and change of usage, effect on surface and ground waters, and air pollution due to fires and dusting. Frequently, these requirements are contradictory. For example, a land saving proposal is to store wastes in mined-out sand pits; but, in turn, those same sites afford the greatest hazard for groundwater pollution. Groundwater is taken from the same geological structures for potable purposes (buried glacial valleys). The environmental study must be approved by various local or regional authorities (Site Planning, Agriculture, Forestry, Environmental Protection, Health and Epidemiology. Most controversial disposal sites are discussed also by local or regional Representative Councils, which supervise the administration. In addition, the five years Site Planning Programs are exposed for public comment in every municipal office; thus, a permit for a new wastes disposal site is very difficult and time consuming to obtain. To satisfy environmental requirements, a number of research programs are under way with subsequent implemention dependent upon the results of the research. The main topics are as follows:

- Construction of large central disposal sites in place of several local ones, to save land and to improve environmental control.
- New technologies using belt

conveyers and spreaders (ZGOT -100) to reach higher elevations and 20 percent more capacity for a disposal site. Material is stored layer by layer and each layer is compacted, thus the fire hazard is reduced (less penetration of oxygen) and water percolation while shaping the slopes for reclamation consistent with the future use of the land.

- Evaluation of pollutants leaching from wastes to ground and surface waters; migration of these pollutants in the water environment; and construction of sealed disposal sites or those with closed water circulation.
- Estimation of dust emission with a specially developed air tunnel-type device to measure emission rate and size of drifted particals at different wind velocities and to determine their mineral composition. This device also makes it possible to evaluate the efficiency of different reclamation methods. Special computer software has been developed to determine dust-in-air migration and dust emission on the adjacent areas.
- Reclamation of the disposal sites with the intended use of the land for agriculture, forestry, and recreation.

As can be seen, the situation in Poland demands strict regulations be enforced and large efforts for the improvement of mining wastes disposal procedures. Although an environmental effect from such disposal sites is inevitable, the effect can be reduced in degree and limited in time.

United Kingdom

In the U.K., the mining wastes are mainly coal wastes (4). As a result of several hundred years, many billion tons of coal wastes have been placed on the disposal sites. Some 100 million tons are received annually. Disposal comes under very strict regulations concerning environmental protection, notably the Control of Pollution Act (1974), Deposit of Poisonous Waste Act (1972) and a number of other regulations which are very strictly enforced. A tremendous amount of work also has been done for the reclamation of old disposal sites. For example, the Midland Region has had a carefully planned project. Landscape is reclaimed with consideration for local conditions, including hedges, stone walls, etc. Thousands of hectares have been reclaimed using these excellent techniques. Presently, the main reclamation efforts tend to utilize coal mining wastes for various purposes, such as:

- road embankments (the Transport Ministry has issued Technical Memoranda approving coal waste utilization on Government contracts),
- railway embankments (progress has been recently observed in this field, though British Rail specifications differ from those of the Transport Department),
- hydrotechnics (canals, rivers, seashore defenses; (requires a careful selection of wastes in view of the type of application),

- reservoirs (settling ponds and preliminary work concerned with the use of coal wastes for the construction of water retaining structures)
- for impermeable lining of more harmful wastes disposal sites (coal wastes in the UK are highly impermeable)
- restoration of depressed areas (old excavations) or damaged areas - admixture to the concretes for making minor roads, parking sites, etc.
- reinforced soil structures
- light weight aggregates
- building blocks
- brick making
- admixtures to cement.

When the coal wastes are impossible to utilize and subsequently must be stored, the Environmental Impact Assessment (EIA) is necessary to identify the negative effects of disposal and the methods of utilization and reclamation as well (5). The study should stress the change in land use and the agricultural management of dumping grounds. EIA comprises adequate blank forms which, when completed, allow a comparison between different alternatives and make a basis for discussions with local authorities. At a regional level, it is intended to identify disadvantages which can result from a change in the land use.

USSR

Currently, some 1400 under- ground mines and more than 6300 open pits are in operation for the extraction of mineral products. In general, the area damaged by mining is about 1.3 million hectares (without peat-land). The national economy's demand for mineral products and fuels over the next 10-15 year period will require additional mining on an area of greater than 1 million hectares. About twenty percent of this area is for mine waste disposal sites. The mining wastes are broken up into three groups: solid, liquid and volatile wastes. In 1975, the yield of wastes and sterile rock in mining all over the country attained 8 billion tons and 98% of this volume was dumped to the disposal sites. The area covered by disposal increases year by year because the useful mineral content in the mined material decreases due to deterioration of geologic conditions. The mining wastes disposal sites and spoil heaps in Krivbass can be given here as an example. They cover an area of above 16,000 hectares where more than 2 billion m3 of wastes from iron ore upgrading are placed. In the Ural ore mining region, one fourth of the mined ore is dumped on to the disposal sites. A share of capital costs for construction of disposal sites comprises 8-10 percent and 2 percent of the labor cost is allocated to their maintenance.

In the USSR, legal regulations are valid concerning protection of useful mineral resources. Rules on how to turn over these resources to the user are proscribed and fundamental rights and duties of the user are defined. Mining permits are issued by a Republican or

Territorial Inspector of Mines, after having been agreed upon with the supervisory services of the USSR's Ministry of Geology. A company receives a mining permit where its duties concerning the correct utilization of minerals including waste disposal are specified. In the planning and designing of mines, up to 20 percent of the area of withdrawn land is assigned for the overburden and wastes disposals. Sterile rocks and wastes are used for back-filling of workings, railway embankments and production of building materials and structures. However, it is less than 2 percent of the total volume. A present day trend is to manage the mining wastes problem in four directions: 1) reduction of mining solid waste volume through improvement of mining operations, 2) use of mining wastes during mining operations, 3) development of minerals treatment processes to make use of all mineral products, and 4) mining wastes utilization in the accompanying productions and branches of national economy. In the USSR, extensive research is conducted in the field of hydrogeochemistry; many of the results find their application in determining effects of mining wastes disposal on groundwater. Research centers in Moscow and Leningrad are the leading ones in this field, and F.M. Boczewier, A.E. Oradowska, P.J. Polubarinowa-Koczina, W.N. Szestakow, N.V. Weregin and W.A. Mironienko have the most interesting achievements.

Other Countries

In some other European countries, mining wastes disposal is still taken very liberally. For example, in Spain, mining wastes are dumped into the sea and reclamation is not strictly required. Similar situations exist in Yugoslavia and in Greece. These countries have just started to talk about detrimental effects arising from such procedures and about the necessity of tightening restrictions in the field.

In the African countries, no environmental requirements are valid in practice. Only the most drastic violations (e.g., waste disposal up-stream of the river where water intakes for a city are located below) are criticized and preliminary discussions on their necessary constraint are slow in starting. A similar situation occurs in the countries of Southern Asia, from Turkey through Iraq, Iran, India, Thailand to Malaysia, and in Oceania as well. In Papua-New Guinea for example, the Government has shares in the mineral investments and as shareholder, assumes a liberal attitude towards the action for environmental regulations because this increases the costs of projects.

In those countries, no research on the environmental effect of mining wastes is being conducted, although such research has been undertaken recently in some countries such as Spain, Yugoslavia, India. The United Nations

Environment Program developed the recommendations for environmental protection in mining, including some recommendations for mining wastes disposal sites, and disseminated them to all governments in the early 1980's. The aim was to help the governments of Third World countries but the action was not as successful as had been expected.

SUMMARY

1. Definition of solid mining wastes is not clear. In some countries overburden from open pit operations is considered as wastes (Australia) and in others where it consists of sands and clays (Poland, Germany) as non-waste material. In the world scale the output of solid mining wastes is 15 to 20 million tons per year.

2. Huge disposals of solid mining wastes, despite mostly low concentration of harmful components, effect considerable impact on the land use, as well as pollution of surface, groundwater and air.

3. The legal status of solid mining wastes disposal is very different in various countries - from very strict to very liberal. The strictness of regulations depends mostly on the economical situation, but also on the relations of mining to urbanized areas. Rich countries with dispersed mining are more liberal than poorer countries with concentrated operations. Often the execution of legislation is more liberal than the regulations. Permits for new disposal sites are always more difficult than operation of under old permits.

4. The research on solid mining wastes disposal sites in advanced countries with concentrated mining is now more oriented toward environmentally accepted utilization of those wastes (due to shortage of land). In advanced countries with dispersed mining is oriented more toward environmental aspects of disposals. The real research in this field is carried in about 20 countries.

5. As the understanding of environmental hazards produced by solid mining wastes disposal is disseminated around the world, it should be expected that it will be strictly regulated until the end of this decade in economically advanced countries and until the end of the next decade all over the world.

REFERENCES

1. Schmidt H.G., 1984. The activities of a Regional Administrative Union of Municipalities of a Coal Mining District the Field of Reclamation, Treatment, and Utilization of Mining Wastes. Proceeding of the Symposium of National Coal Board Minestone Executive. Durham, England 1984.

2. Empfehlungen fur das Auf und Abhalden vonSteinkhlen aufnicht standig genutzen Lagern. 1975. FRGBB 23015.

3. Libick J., Niemcewicz J.1985, Construction of Large Coal Waste and Power Plant Ash Disposal in View of Environmental Protection Proceedings of International Congress on Wastes Utilization. Katowice, Poland, 1985.

4. Turnbull d., 1984, the Role of the Minestone Executive in British Mining and Civil Engineering Proceedings of the Symposium of National Coal Board Minestone Executive, Durham, England 1984.

5. Selman, P. H., 1984. Environmental Assesments of Projects and Plans. Method for the Strategic Appraisal of Waste Disposal Impacts. Proceedings of the Symposium of National Coal Board Minestone Executive. Durham, England 1984.

6. Mosintz, W.N. - Okhrana Okrujushtshey Sredie Pree Proyectovanyu y Expolataciy Rudnikov. Moscow, 1981.

DISCLAIMER

The work described in this paper was not funded by the U. S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

DISTRIBUTION OF FLOW RATES AND TRACER BREAKTHROUGH TIMES IN FIELD SOIL

Andrew S. Rogowski
USDA-ARS, Northeast Watershed Research Center
University Park, PA 16802

ABSTRACT

An experimental 0.3 m thick clay liner was ponded for 1 year. During that time inflow, outflow and change in density were routinely monitored at 250 locations. Results suggest that initial increase and final leveling off of the density values could be associated with water passing into the clay matrix. Increase in density was accompanied by increased outflow which subsequently declined and leveled off at twelve months. These changes were associated with leaching and precipitation of Fe and Mn and method of computation. Tracer breakthrough times were consistently faster than water flow rates, although initial water breakthrough times following ponding were similar to tracer breakthrough times. Results suggest that water and solutes moved in the clay through a small portion of total porosity only.

INTRODUCTION

Relationship between laboratory measurements and field transport of water and solutes through compacted clay liners have become a focus of attention (3). Although commonly used liner evaluation criteria include flow measurement on core samples, such measurements seldom if ever represent the permeability of the liner as a whole, which may be as much as several orders of magnitude different from lab values. While some organic and inorganic chemicals that react with the clay matrix have a profound influence on permeability characteristics of compacted clays (2), most solutes that do not react with the clay matrix are assumed to move through at the same rate as water (5). There is, however, sufficient evidence in literature (15) to show that this is not always the case. Breakthrough times appear to be faster and arrival concentrations higher than what would be predicted on the basis of apparent water flux.

PURPOSE

In the early stages of this study a survey of literature was carried out (8), experimental facility was constructed, and a clay liner and instrumentation were installed using industry methods and equipment. Preliminary results are given in (9) and (10). Subsequently, an updated report on liner performance was prepared (11), and two other publications dealt with chemical composition of outflow (12) and variability considerations (13). In this paper, based on one year of data, distribution of average water flux in time

Preceding page blank

and in space will be considered along with transport of Br^- tracer at selected locations.

The primary objective of this study was to evaluate spatial and temporal distributions of outflow in a compacted experimental clay liner large enough to be considered representative of a field site. The secondary objectives were to examine the fate of introduced tracer at selected locations, to evaluate monitored outflow in surrounding drains and to compute travel times, flow pathways, and breakthrough concentrations.

APPROACH

The testing facility consisted of a bridge-like 9 x 23 m (30' x 75') reinforced concrete platform shown in Figure 1. A 0.9 x 0.9 m (3' x 3') grid of leachate collection drains underlying compacted soil was complemented by a 0.9 x 0.9 m (3' x 3') grid of 0.3 m (11") diameter buffered infiltration cylinders at the surface. Figure 2 shows the sampling grids used in the study, their origin (0,A) was the southwest corner of the platform.

Imbedded in the floor of the platform and positioned horizontally across the facility were the lower of the 24 access tubes for the measurement of density using the Troxler[1] dual gamma probe. Positioned on the clay surface and situated exactly 0.3 m (1') above the lower access tubes were the upper access tubes. The attenuation measurements were made on a 0.9 x 0.9 m (3' x 3')

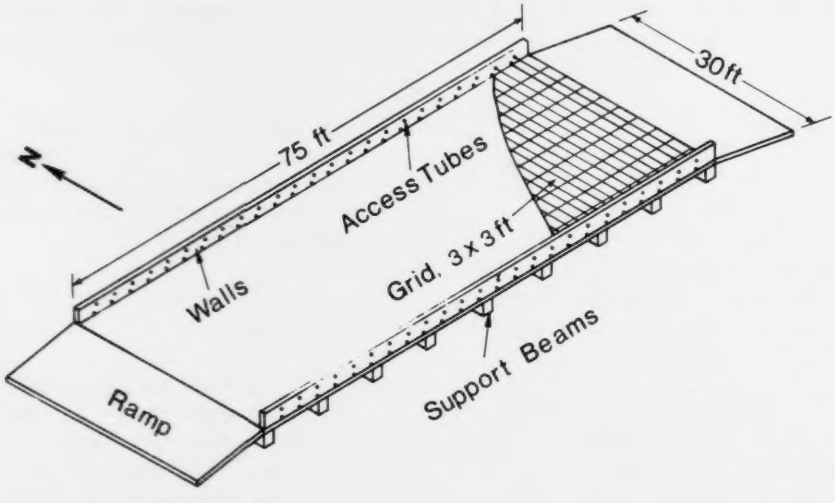


Figure 1. Clay liner testing facility.

---

[1] The mention of trade names in this publication does not constitute an endorsement of the product by the U.S. Department of Agriculture over other products not mentioned.

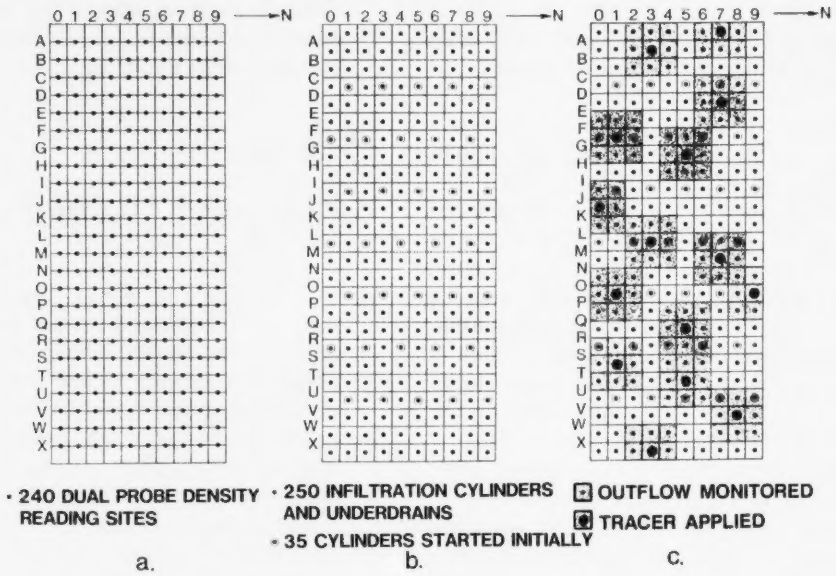

0 1 2 3 4 5 6 7 8 9 → N
A B C D E F G H I J K L M N O P Q R S T U V W X
• 240 DUAL PROBE DENSITY READING SITES
a.
• 250 INFILTRATION CYLINDERS AND UNDERDRAINS
• 35 CYLINDERS STARTED INITIALLY
b.
OUTFLOW MONITORED
TRACER APPLIED
c.

Figure 2. Experimental 3 x 3 ft (0.91 x 0.91 m) grids used in measuring (a) bulk density, (b) infiltration and outflow, (c) tracer breakthrough.

grid with a gamma source (Cs^{137}) in the lower tube and the detector in the upper tube. The degree of attenuation was used to compute wet density, or changes in wet density in a conical volume of soil between the source and the detector.

Clay soil (Typic hapludult) used as the liner material was the B-horizon of a commercially available cherty silt loam from central Pennsylvania. It was compacted wet of optimum to greater than 90% Standard Proctor (8), it is classified as a CL type having a permeability of 1.10 to 1.76 x 10^{-8} cm/sec as determined in the laboratory with a falling head permeameter at 90% maximum density and a gradient of about 20. Mineralogically the soil mineralogy is dominated by a mixture of illite and kaolinite with minor amounts of montmorillonite.

After the liner was constructed, instrumented and ponded, water level was maintained constant with an automatic constant head tank. Similarly, each of the infiltration cylinders and evaporation pans were equipped with 1 litre Mariotte constant head bottles set to the same level as in the ponded water outside. Individual leachate drains were routed to the outside of the platform and leachate was collected in appropriately sized containers. Simultaneous readings of water level changes in a grid of evaporation pans gave the necessary correction to be applied to ring infiltration data. Corresponding to each set of ring and drain data (Figure 2b) a set of wet density readings was taken (Figure 2a) with the Troxler[1] dual gamma probe.

Collection of infiltration, leachate and evaporation data began immediately after ponding (9). Initially, the data were collected daily with subsequent transition to weekly intervals. Soon after ponding it became apparent that the infiltration cylinders and leachate drains situated next to the sidewalls in lower density zones were responsible for a large portion of infiltration and drainage. The leachate from all drains near the sidewalls was therefore isolated, combined into one sump and measured separately from the central matrix of 184 remaining individual drains and rings.

Tracer studies were initiated at the conclusion of the main experiment. To prepare the tracer, 1 gram molecular weight of KBr (119.0 g) was dissolved in 1L of water to give 1M solution of Br^- (79.9 g/L). Either 50 or 100 mℓ of this solution were diluted with ponded water to 2000 mℓ and added to 15 rings (Figure 2c) in one, two, or three 2000 mℓ increments depending on the hydraulic flux rate and expected travel times. At the time tracer solution was applied to rings initial (time = 0) samples of leachate from underlying drain and 8 (or 5) surrounding drains were taken. Sampling of leachate was continued at suitable intervals depending on the volume of accumulated outflow. Leachate samples were analyzed for Br^- content using ion specific bromide electrode.

The data were analyzed using geostatistical techniques of structural analysis and kriging. Kriging provides minimum variance estimates of a property over an area, and variogram analysis delineates the extent of structural dependence of parameters studied.

RESULTS

Distribution of Density and Outflow in Time

Figure 3 shows changes in mean wet bulk density observed in the soil and contains chronology of events from one month after it was laid down and compacted (10/30/84) through ponding on 3/26/85 and finally draining on 7/23/86. A rapid increase in density after ponding followed by a more gradual rise for the next 9 months could be indicative of progressive soil matrix saturation. At the time of ponding average moisture content averaged 18.1% by weight, while moisture contents after the liner was drained and 3" cores were removed for analysis averaged 18.5%. The 0.4% change in moisture content by weight translates to only about 7 kg/m^3 increase in density, considerably less then the average 60 kg/m^3 increase shown in Figure 3. Could the swelling against the upper access tubes with accompanying compaction be responsible? On the average, vertical swelling of the liner was found to be on the order of 1 to 2 mm, hardly enough to materially increase compaction. We must therefore conclude that although on the average water content changes were only 0.4% by weight enough locations changed 3.5% or more to account for the 60 kg/m^3 changes in density. A clue to what might have happened comes from Veihmeier tube samples taken immediately after ponded water was withdrawn. These gave water contents as high as 25% by weight for some locations where water was observed

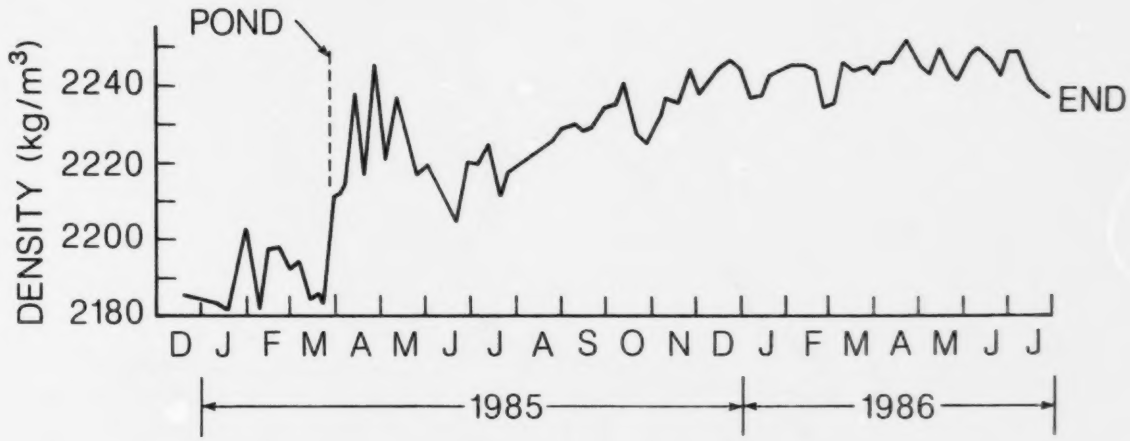


Figure 3. Average density (wet) measured with dual gamma probe.

standing in the tube holes after the sample was removed. Discrepancy between Veihmeier samples and 3" cores suggests initial slow drainage of macropore matrix as opposed to little or no changes in the micropore matrix. Large fluctuations in density between (3/85 to 5/85) necessitated probe repair. Subsequently, a gradual increase in density continued through the first half of 3/86 when readings stabilized. Fluctuations from 3/86 until the end are only slightly larger than experimental error which allows standard count to vary within ± 200 cpm or ± 8.7 kg/m^3.

Figure 4 shows the average outflow rate during the study period. The upper curve represents the outer 66 drains along the walls and the lower curve shows the inner 184 drains. The two are distinguished by differences in the extent of compaction. The inner zone was compacted with a crawler tractor and sheepsfoot roller while a small vibratory roller and jackhammer were used in the outer zone. Values beyond 4/86 reflect other studies conducted on the liner, such as chemical sampling (11) and tracer studies, when Br$^-$ tracer was added. An increasing infiltration rate (12) in the first nine months after ponding could signify increasing matrix saturation and replacement of pore air with infiltrating water. As we have seen however, micropore matrix water content change was only 0.4% by weight. The apparent increase in outflow rate shown requires therefore an alternate explanation. In flooded sediments (1, 14) decomposition of organic matter (i.e., layer of burlap below the clay) proceeds at a slower rate. The end products of metabolism as well as microorganisms responsible differ from those found at well aerated sites. The dominant species are the anaerobic bacteria. The change from aerobic to anaerobic metabolism leads to depletion of O_2 and a shift towards a more negative oxidation reduction potential. Under these conditions soil manganese and iron are reduced and their solubilities increase. Since pH of our soil is 4.2 ± 0.4, ferrous iron can

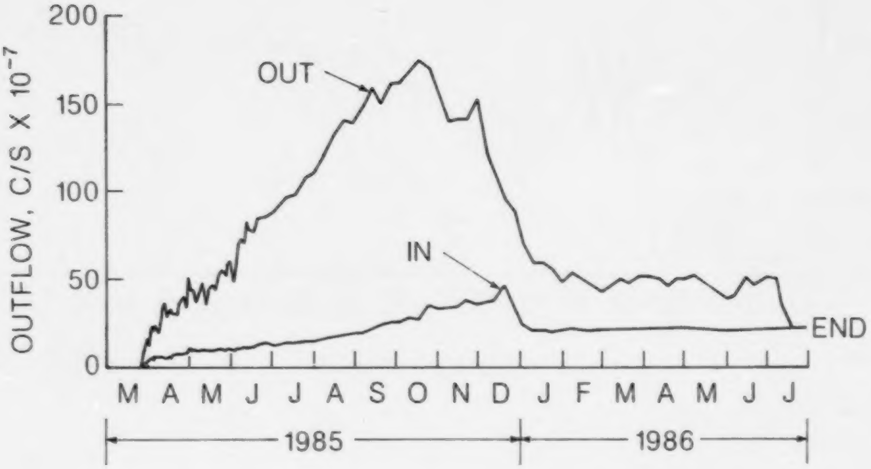


Figure 4. Average outflow rate during a one-year study period.

replace and enhance leaching of Ca^{2+}, Mg^{2+}, and K^+ from the clay. If the soil is reaerated (i.e., through platform drains), oxidized iron and manganese will precipitate, and exchangeable hydrogen (if not neutralized by excess bicarbonate) may dissolve parts of the clay lattice structure decreasing overall stability. Such reactions can lead to internal rearrangement of pore geometry and changes in hydraulic conductivity with time. Significantly, the increase and decline were more noticeable in outflow drains and liner as a whole then in the ring infiltration data (not shown). Corings after the liner was drained revealed very black organic looking sand layer under the clay with little or no trace of burlap, while examination of outflow drains showed close correspondence between drains containing large amount of Fe and Mn precipitates and the spatial distribution of high outflows. Conversely, drains with little, or no precipitate were in areas of very low outflow (< 10^{-7} cm/sec).

Distribution of Outflow in Space

Figure 5 shows areal distributions of outflow fluxes for drains using one year data summation, where total outflow for a given drain is divided by total elapsed time. Orientation (North) here is the same as in Figure 2. Dark areas signify zones in which the flux was less than 10^{-7} cm/sec and white areas zones where flux was greater than 10^{-5} cm/sec. Bar graph to the right of the figure shows relative magnitudes of average fluxes obtained using raw data values. Resultant mean flux was 24 x 10^{-7} cm/sec compared to 14 x 10^{-7} cm/sec when measured at 3 months and 22 x 10^{-7} for the week ending on 4/30/86. The summation results for twelve months and the week ending 4/30/86 were almost

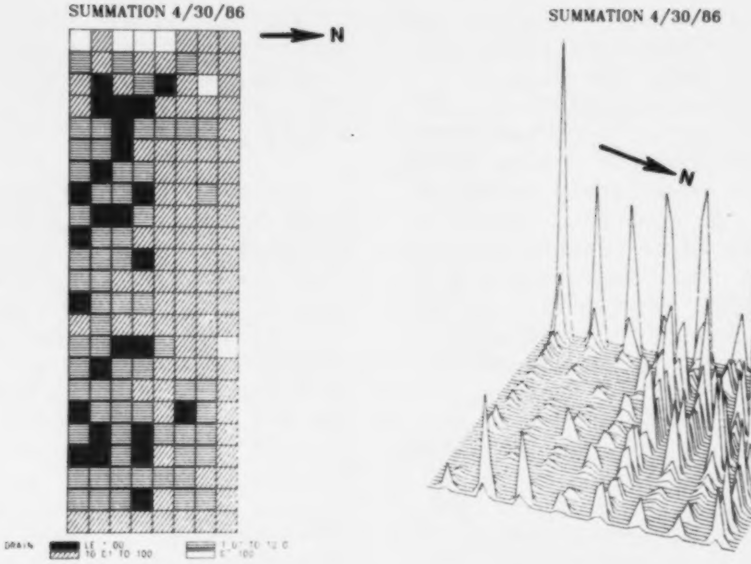


Figure 5. Outflow flux x 10^{-7} cm/sec, drains, raw data, one year summation.

logmormally distributed, and the mean flux evaluated on the basis of log transformed data was 16 x 10^{-7}. The flux at three months was not lognormally distributed. Using a log transformed mean under those circumstances would result in erroneous mean flux value of 4 x 10^{-7} cm/sec. Although it is usually assumed that hydraulic conductivity and flux data follow a lognormal distribution calculated values may indeed be in error unless the lognormality of data values is first verified. It appears that infiltration and outflow in clay need to stabilize before reliable response values are obtained. How long that may take would likely depend on individual cases. In our 0.3 m (1 foot) thick liner it took about 10 to 12 months.

When 12 month outflow values were kriged their mean increased on the average 20 percent, while the variance declined anywhere from 30 to 50 percent. For the log transformed data where applicable, the mean stayed about the same while decline in variance was quite similar to the untransformed data. Variogram analysis suggested that the range for the log transformed data is approximately one-half that of the untransformed values with the sill variance explaining only about one-half of the random variation (nugget effect) present on the scale smaller than the range (4). From variogram analysis a continuity range for hydraulic conductivity was found to be about 10 m (30 ft), and kriging estimates were observed to have a variance of (14 to 25 x 10^{-7} cm/sec)^2. Advantage of geostatistics in spatial interpolation lies in its ability to provide optimal (minimum variance) estimates of spatially distributed values.

Tracer Studies

In Figures 6 and 7 relative concentrations of tracer are shown for drain clusters under the ring to which Br^- solution was applied. In Figure 6 breakthrough occurred first through one of the side drains rather than the drain immediately below the spiked ring. In contrast, Figure 7 shows the case where breakthrough occurred in the drain immediately below the spiked ring. Sensitivity of the measuring technique declines with decreasing concentration and values below 10^{-4} C/Co are not included. For the A3 cluster (Figure 6) most of the C/Co concentrations are larger then 10^{-4} C/Co, while for the G5 cluster very many are smaller. For both clusters, but more so for the G5 there appears to be one primary contributing drain with several lesser contributions from surrounding drains. The data were not in the form of classical curve, probably because insufficient time has elapsed. However, since G5 recovery approached 85% a step function type of curve, suggesting macropore flow, is likely.

Figures 8 and 9 illustrate cumulative leachate concentration of Br^- as a function of time (hrs) for the same drain clusters as shown in Figures 6 and 7, and Table 1 shows breakthrough times, and amounts of tracer recovered for all sites. Recoveries as high as 84% for G5 site and 43% for A3 site suggest that only a small fraction of total porosity acts as a conduit for water moving through the clay. Results also suggest existence of primary pathways to G5 and A4 drains and several lesser secondary pathways through which about 1% of the tracer moves. In Table 1 tabulated outflow rates for

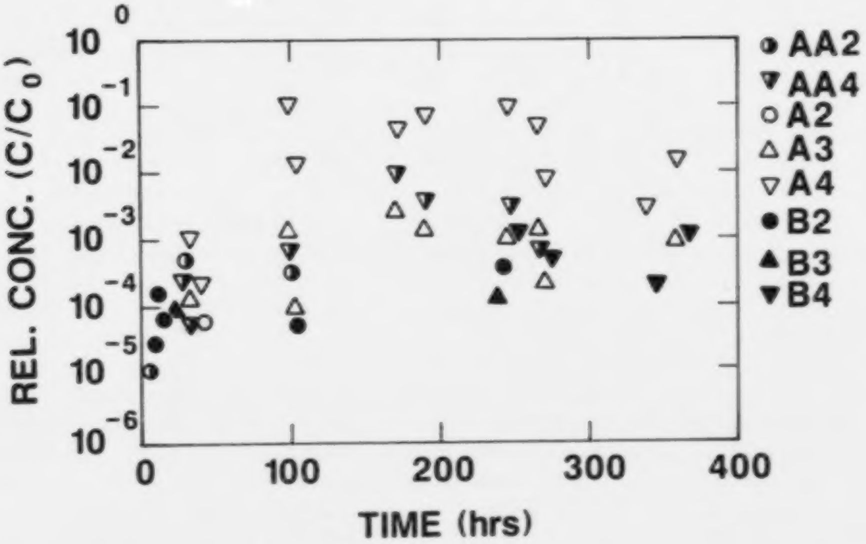


Figure 6. Relative concentration of Br^- in outflow from underlying △ A3, and surrounding ◑ AA2, ▼ AA4, o A2, △ A3, ▽ A4, ● B2, ▲ B3 and ▼ B4 drains below the ring to which tracer was applied.

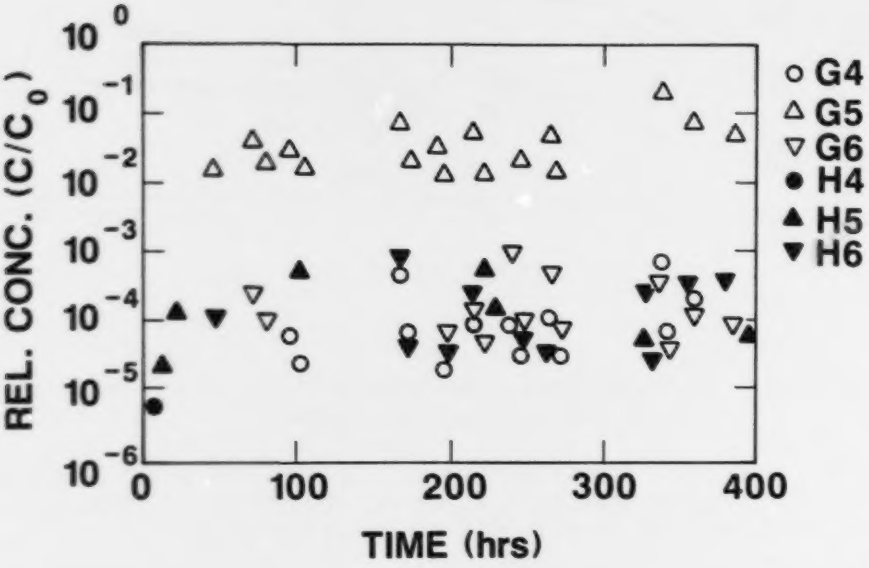


Figure 7. Relative concentration of Br$^-$ in outflow from underlying Δ G5, and surrounding o G4, ∇ G6, ● H4, ▲ H5, and ▼ H6 drains below the ring to which tracer was applied.

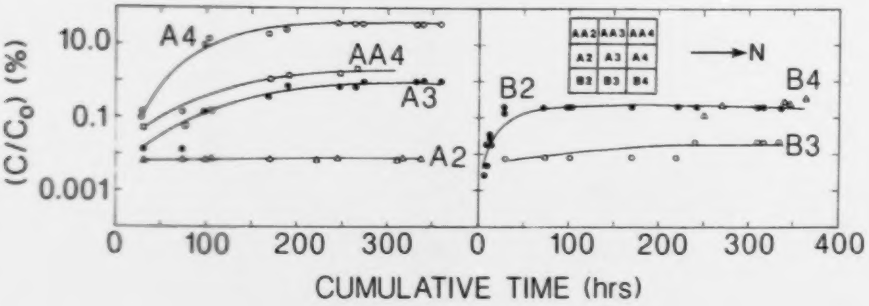


Figure 8. Relative cumulative concentration of Br$^-$ in leachate from A3 and surrounding drains.

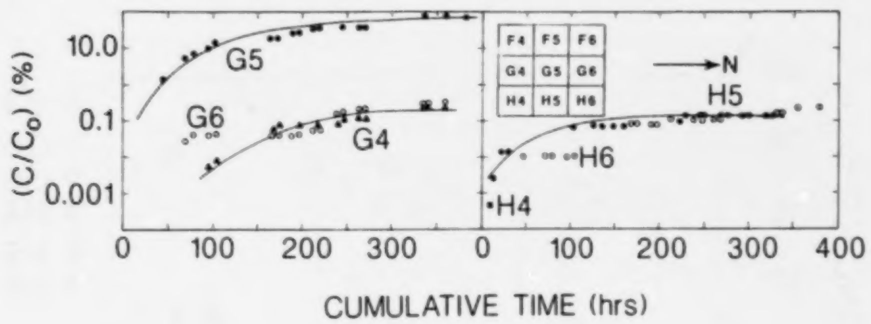


Figure 9. Relative cumulative concentration of Br^- in leachate from G5 and surrounding drains.

TABLE 1. Breakthrough times for Br^- tracer and water[1], cumulative tracer concentration (C/Co) recovered and flux outflow rate for a drain subtending spiked ring.

Ring	Breakthrough Tracer	Breakthrough Water	C/Co	Flux Rate
	hrs	hrs	%	10^{-7} cm/sec
AA7	26	48	5	11
A3	30	24	43	80
D7	29	144	24	26
F1	25	192	2	19
G5	47	144	84	19
J0	170	48	2	11
L3[2]	>265	158	2	2
M7	53	72	29	35
01	48	312	<1	9
09	48	48	10	8
Q5	7	144	4	138
S1	54	312	2	2
T5	161	192	1	19
V8	167	144	3	14
X3	25	144	6	33

[1] Approximate breakthrough times for water following ponding on 3/26/85, drains checked for outflow twice on the first day after ponding then at 2, 3, 6, 7, 8, 9, 10, 13 and 15 days.

[2] Breakthrough at M2, M3 and M4 at 7 hrs none at L3.

drains corresponding to drains under the ring to which tracer Br^- was applied are shown. If we were to assume that a tracer travels in a straight 0.3 m long path from i.e., ring G5 to drain G5 its travel time appears to be considerably faster than the measured flux rate. Various explanations could be advanced for the discrepancy with perhaps the most plausible being anion exclusion which tends to reduce cross sectional area available for Br^- transport particularly at pH values of leachate (pH 8) observed in our study (11). An alternate explanation may be that although both water and tracer move at a similar rate they move only through a small fraction of total porosity. Our early records indicate that for the G5 drain cluster outflow began about 144 hours after ponding compared to 47 hours for tracer breakthrough, and for A3 drain cluster it began about 24 hours after ponding compared to 30 hours for tracer breakthrough. The discrepancy between the flux rates computed from outflow volumes and breakthrough times appears to be in the method of defining the flux density (6) as the unit volume of water (cm^3) passing through unit area (cm^2) in unit time (sec.). From a practical point of view, even if design criteria for a clay liner are met (flux rate of 10^{-7} cm/sec or better), true travel times for water and associated solutes may be several orders of magnitude higher because the effective porosity through which the transport actually takes place is on the order of 0.1 or less of the total porosity.

ACKNOWLEDGMENTS

The support of this study by U.S. EPA, through Interagency Agreement No. DW12930303-01-0 with USDA is acknowledged.

REFERENCES

1. Bouma, J., 1983, Hydrology and Soil Genesis of Soils with Aquatic Moisture Regimes, In: Pedogenesis and Soil Taxonomy 1. Concepts and Interactions, L.P. Wilding, N.E. Smeek, and G.F. Hall (eds.), pp. 253-279.

2. Brown, K.W., and D.C. Anderson, 1983, Effects of Organic Solvents on the Permeability of Clay Soils, EPA-600/2-83-016, U.S. EPA, Cincinnati, OH, 153 p.

3. Daniel, D.A., 1985, Clay Liners Where Do We Go from Here? In: Proceedings, International Conference on New Frontiers for Hazardous Waste Management, September, EPA-600/9-85/025, U.S. EPA, Cincinnati, OH, pp. 266-273.

4. Journel, A.G., and Ch.J. Huijbregts, 1978, Mining Geostatistics, Academic Press, NY, 600 p.

5. Jury, W.A., 1982, Simulation of Solute Transport Using a Transfer Function Model, Water Resour. Res., Vol. 18, No. 2, pp. 363-368.

6. Kirkham D., and W.L. Powers, 1972, Advanced Soil Physics, Wiley Interscience, NY, 534 p.

7. Nye, P.H., and P.B. Tinker, 1977, Solute Movement in the Soil-Root System, Univ. of California Press, Los Angeles, CA, 342 p.

8. Rogowski, A.S., and E.B. Richie, 1984, Relationship of Laboratory and Field Determined Hydraulic

Conductivity in Compacted Clay Soils, In: Proceedings, 16th Mid-Atlantic Industrial Waste Conference, M.D. LaGrega and D.A. Long (eds.), Technomic Publ. Co., Inc., Lancaster, PA 17604.

9. Rogowski, A.S., 1985, Effectiveness of a Compacted Clay Liner in Preventing Ground Water Contamination, In: Proceedings, 5th National Symposium on Aquifer Restoration and Ground Water Monitoring, May, National Water Well Assn., Worthington, OH, pp. 412-429.

10. Rogowski, A.S., B.E. Weinrich, and D.E. Simmons, 1985, Permeability Assessment in a Compacted Clay Liner, In: Proceedings, 8th Annual Madison Waste Conference, September, Univ. of Wisconsin, Madison, WI, pp. 315-336.

11. Rogowski, A.S., 1986, Hydraulic Conductivity of Compacted Clay Soils, In: Proceedings, 12th Annual Research Symposium, EPA-600/9-86/022, U.S. EPA, Cincinnati, OH, pp. 29-39.

12. Rogowski, A.S., 1986b, Degree of Saturation, Hydraulic Conductivity and Leachate Quality in a Compacted Clay Liner, In: Ground Water Hydrology, Contamination, and Remediation, R.M. Khanbilvardi and J. Fillos (eds.), Scientific Publications Co., Washington, DC, pp. 339-353.

13. Rogowski, A.S., D.E. Simmons, and B.E. Weinrich, 1987, Variability of Infiltration in a Clay Layer of a Typic Hapludult, In: Proceedings, International Conference on Infiltration, Development and Application, Yu-Si Fok (ed.), Univ. of Hawaii at Manoa, Honolulu, HI, pp. 502-525.

14. Stevenson, F.J., 1985, Cycles of Soil Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients, John Wiley & Sons, NY, 380 p.

15. White, R.E., 1985, The Influence of Macropores on the Transport of Dissolved and Suspended Matter through Soil, In: Advances in Soil Science, B.A. Stewart (ed.), Springer Verlag, NY, Vol. 3.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

STABILIZATION OF ENZYMES USED TO DEGRADE PESTICIDES

Daniel R. Coleman, F. Reese Frazer, Douglas B. Rivers,
Thomas R. Tice, Thomas O. Dappert, David W. Mason
Southern Research Institute
Birmingham, AL 35255-5305

ABSTRACT

As the active ingredients of formulations used to decontaminate soil and equipment contaminated with toxic materials such as pesticides, enzymes offer several inherent advantages and, certainly, some limitations. Because of the catalytic nature of enzymes, each molecule of enzyme could destroy countless molecules of the contaminating toxic compound. Moreover, this destruction takes place under mild conditions of temperature, pressure, and solvent. The principal limitation in the use of enzymes is the inherent instability of many enzymes, during both storage and application. Our studies have been directed toward developing an enzyme preparation which is stabilized against extremes of pH, temperature, and exposure to organic solvents. Using the model enzyme subtilisin, we have investigated several stabilizing methods including crosslinking, gel entrapment, covalent attachment, and microencapsulation. The stabilities of these preparations have been determined in various decontaminating formulations.

INTRODUCTION

Covalent Crosslinking

Covalent crosslinking is a well-documented method of stabilizing enzymes (1,2). We have studied the stabilization of subtilisin by crosslinking with glutaraldehyde. Commercially available glutaraldehyde contains essentially no free glutaraldehyde but consists of a complex mixture of polymeric material (3). The reaction of glutaraldehyde with crystalline enzymes is rapid in aqueous solutions at room temperature. The crosslinked enzyme should withstand wide ranges of pH, ionic strength, and temperature (3). A schematic illustration of crosslinked enzyme molecules is shown in Figure 1.

Covalent Attachment

Covalent attachment of enzymes to polymeric supports has been shown to stabilize enzymes against denaturation (4). This stabilization presumably occurs because of multiple attachments between the enzyme and support, which prevents conformational changes that cause a loss of activity. We are evaluating the covalent attachment of subtilisin onto a commercial preparation consisting of 6% crosslinked agarose beads that have been derivatized

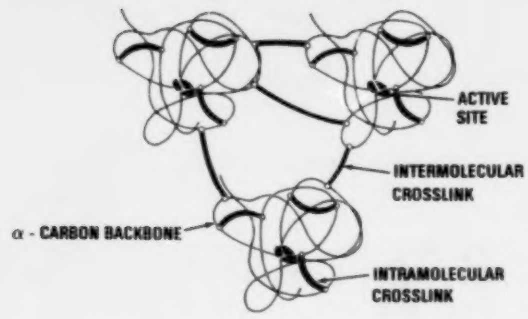


Figure 1. Enzyme molecules crosslinked with glutaraldehyde.

with 1,1'-carbonyl diimidazole to give a highly activated imidazolyl/carbamate matrix. The pendent amino groups of the enzyme react with the activated support to form a covalent attachment. The covalent attachment of an enzyme molecule to a polymeric support is shown in Figure 2.

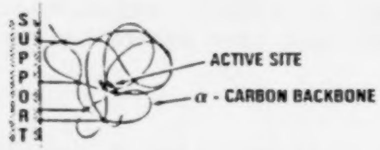


Figure 2. Enzyme molecule attached to an insoluble support.

Microencapsulation

Microencapsulation has been used to stabilize enzymes by providing a selectively permeable barrier between the enzyme and the environment. This technique involves coating the enzyme with a polymeric material that is selectively permeable to pesticides (Figure 3). The enzyme can be encapsulated as a dry powder or in an aqueous environment.

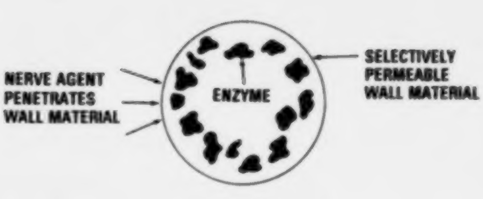

NERVE AGENT PENETRATES WALL MATERIAL
ENZYME
SELECTIVELY PERMEABLE WALL MATERIAL

Figure 3. Schematic illustration of microencapsulated enzyme.

We have evaluated microencapsulation as a method of stabilizing horseradish peroxidase (HRP). The HRP is a model system to determine the stability provided by microencapsulation in the presence of a nonspecific protease, Pronase E. Nonproteolytic HRP allows us to easily distinguish between proteolytic Pronase E and nonproteolytic HRP enzyme activity. Microencapsulation appears to provide the required protection of HRP from proteolytic degradation.

Gel Entrapment

Gel entrapment is a convenient, inexpensive way to stabilize enzymes by simple physical containment combined with covalent attachment of the enzyme to the gel. The gel-entrapment procedure we used involves chemical modification of the enzyme with a bifunctional monomer followed by copolymerization of the modified enzyme with another monomer (5). In the final preparation, the enzyme is attached to a support which has a surface geometry congruent to that of the enzyme. This process is illustrated in Figure 4.

MATERIALS AND METHODS

Assay Procedure

The pH-stat assay used to measure subtilisin activity is a modification of the procedure described by Ottesen and Svendsen (6).

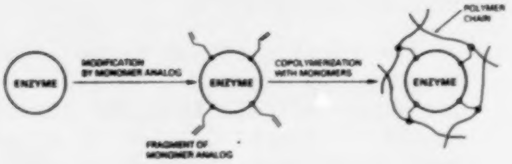

ENZYME
MODIFICATION BY MONOMER ANALOG
ENZYME
FRAGMENT OF MONOMER ANALOG
COPOLYMERIZATION WITH MONOMERS
ENZYME
POLYMER CHAIN

Figure 4. Enzyme immobilization by copolymerization of a modified enzyme with monomer.

Crosslinking

Subtilisin was crosslinked with glutaraldehyde using a modification of the procedure described by Brown (1) for crosslinking chymotrypsin. We evaluated two glutaraldehyde concentrations, 0.5 and 1.0% (v/v), and two reaction times, 3 and 18 hr. The 3-hr reactions were conducted at room temperature (≈25 °C), while the 18-hr reactions were conducted at 3 °C. After crosslinking, the subtilisin suspensions were assayed to determine the remaining enzyme activity. The suspensions were then lyophilized and weighed to determine the yield of crosslinked enzyme.

Covalent Attachment

Reacti-Gel 6X (Pierce Chemical Co., Rockford, IL) was used as the insoluble support for subtilisin. Subtilisin (10 mg) was immobilized on either 30, 60, or 100 mg of Reacti-Gel to determine an optimum subtilisin/Reacti-Gel ratio. Immobilization was conducted in 12.5 mM borate buffer (pH 10.51) for 19 hr at 4 °C with gentle stirring. The three phases of the protein coupling (supernatant, gel wash, immobilized enzyme) were then assayed to determine the amount of subtilisin activity in each phase.

Microencapsulation

Two types of calcium alginate microcapsules containing HRP were prepared. Both types of microcapsules were prepared with HRP in a calcium alginate gel, which was then coated with a less permeable polymer. Two polymers were employed to coat the alginate gel. The first microcapsules were prepared with sodium alginate and poly(vinyl alcohol). Additional microcapsules were prepared with sodium alginate and poly-L-lysine.

Gel Entrapment

The gel-entrapment procedure we used was based on the procedure described by Martinek et al.(5). Subtilisin was first modified by acryloyl chloride, which acylates the ε-amino groups of the lysyl residues in the enzyme polypeptide chain. The acryloyl chloride-modified enzyme was then entrapped in a polymethacrylate gel.

To entrap subtilisin in polymethacrylate gel, subtilisin (160 mg) was first dissolved in 50 mL of 0.2 M KH_2PO_4 (pH 8.0). The enzyme solution was placed in an isopropanol/dry-ice bath and cooled to less than 5 °C. The enzyme solution was stirred rapidly to prevent freezing. Acryloyl chloride (2.4 mL) was then added slowly to the enzyme solution. While the acryloyl chloride was being added, the pH of the enzyme solution was maintained at about 8.0 by adding an aqueous solution of either saturated or 50% (w/v) KOH. Sodium methacrylate (40 mg) as a monomer and tetramethylethylenediamine 20.5 μL and ammonium persulfate (26 mg) as initiating agents were added. The mixture was next poured into thin-walled test tubes and allowed to polymerize for 24 hr at 3 °C. After the gel polymerized, it was mixed with 25 mL of 5 x 10^{-3} M borate buffer and ground in a tissue homogenizer. The ground gel was poured into a petri dish and dried at 30 °C for 24 hr. The dried gel was recovered and assayed.

RESULTS

Crosslinking

The percentage of subtilisin recovered from each sample shown in Table 1 is based on the weight of the material added initially. The largest amount of subtilisin (28.5%) was recovered from the solution treated with 1.0% glutaraldehyde for 3 hr at room temperature. Subtilisin treated with 0.5% glutaraldehyde did not react sufficiently to cause precipitation of a crosslinked product.

The results of the pH-stat assay are also shown in Table 1. The subtilisin crosslinked with 1.0% glutaraldehyde for 18 hr had the highest activity, 30.5 ± 0.6% of the initial velocity (v_0) of the native subtilisin solution. The v_0 for the subtilisin crosslinked with 1.0% glutaraldehyde for 3 hr at room temperature was 24.0 ± 0.6% of the v_0 of the native enzyme solution.

A loss of activity after subtilisin was crosslinked with glutaraldehyde was expected based upon previous studies with serine proteases other than subtilisin (1). Chymotrypsin crosslinked with glutaraldehyde retained 43.6 to 56.8% of the activity of the native enzyme. The percent of original activity retained by trypsin ranged from 17.6 to 19.0%. The amount of enzyme activity lost during crosslinking is thus within the expected range: however, modification of the crosslinking procedure to determine the set of subtilisin has not been tried. By varying the glutaraldehyde concentration, reaction time, or conditions that are optimal for temperature, improved recovery and increased residual activity of the enzyme may be expected.

Covalent Attachment

The results of the immobilization experiments are shown in Table 2. The data indicate that the optimum amount of Reacti-Gel for 10 mg of subtilisin is between 60 and 100 mg.

Microencapsulation

Three batches of microcapsules were prepared with sodium alginate and poly-L-lysine. These three batches contained poly-L-lysine having molecular weights of 14,000, 59,000, or 90,000 daltons. Horseradish peroxidase (HRP) was the enzyme of choice for a model system for microencapsulation. Following encapsulation, 50% of the HRP activity was located in the microcapsule core, while the remaining HRP activity was bound in the microcapsule wall. The encapsulated HRP was challenged with the nonspecific protease, Pronase E. Within six hours, all HRP activity located in the microcapsule wall was lost. However, all HRP activity located in the microcapsule core was maintained through the 48-hr incubation period. This indicates that microencapsulation may be an effective method of protection from proteases in the environment for enzymes used to degrade pesticides.

Gel Entrapment

The gel-entrapped subtilisin had about 6% of the activity of native subtilisin. Martinek et al. (5) reported that chymotrypsin entrapped in polymethacrylate gel had 30% of the activity of the native enzyme.

Table 1. Assay results for glutaraldehyde-crosslinked subtilisin

Treatment			
Glutaraldehyde concn, %	Incubation time, h	v_0, M/min/mg protein	Activity, %
0	none	6.00 ± 0.22	100.0 ± 3.6
1.0	3	1.44 ± 0.04	24.0 ± 0.6
1.0	18	1.83 ± 0.04	30.5 ± 0.6

Table 2. Subtilisin immobilized on graded concentrations of Reacti-Gel

Test preparation	Sample phase	v_0, M/min/mg protein	Activity, % of control, ± SD	Total activity recovered, % ± SD
Enzyme standard	—	2.71 ± 0.13	100.0 ± 4.8	—
Immobilization control	—	2.35 ± 0.05	86.7 ± 1.9	—
30 mg Reacti-Gel	Supernatant	1.65 ± 0.31	60.9 ± 11.4	96.7 ± 21.7
	Gel wash	0.24 ± 0.03	8.9 ± 1.1	
	Immobilized enzyme	0.73 ± 0.25	26.9 ± 9.2	
60 mg Reacti-Gel	Supernatant	0.75 ± 0.05	27.7 ± 1.8	99.3 ± 22.8
	Gel wash	0.11 ± 0.13	4.1 ± 4.8	
	Immobilized enzyme	1.83 ± 0.44	67.5 ± 16.2	
100 mg Reacti-Gel	Supernatant	0.29 ± 0.05	10.7 ± 1.8	87.1 ± 22.1
	Gel wash	0.12 ± 0.04	4.4 ± 1.5	
	Immobilizied enzyme	1.95 ± 0.51	72.0 ± 18.8	

Because this level is higher than the level of activity we obtained, we plan to conduct additional gel-entrapment experiments to improve our results.

ACKNOWLEDGMENTS

We wish to acknowledge the US Army Chemical Research, Development and Engineering Center for support of this work under Contract DAAA15-85-C-0072.

REFERENCES

1. Brown, G.B. Chemically aggregated enzymes. In: Mosbach, K., ed. Methods in enzymology: v. 44. New York: Academic Press; 1976: 263-280.

2. Wold, F. Bifunctional reagents. In: Hirs, C.H.W.; Timasheff, S.W., eds. Methods in enzymology; v. 25. New York: Academic Press; 1972: 623-651.

3. Richards, F.M.; Knowles, J.R. Glutaraldehyde as a protein crosslinking agent. J. Mol. Biol. 37: 231-233; 1968.

4. Betchell, G.S.; Ayers, J.S.; Hancock, W.S.; Hearn, M.T.W. Novel method of activation of crosslinked agaroses with 1,1'-carbonyldiimidazole which gives

a matrix for affinity chromatography devoid of additional groups. J. Biol. Chem. 254: 2572-2574; 1979.

5. Martinek, K.: Klibanov, A.M.: Goldmacher, V.S.: Besezin, I.V. The principles of enzyme stabilization. I. Increase in thermostability of enzymes covalently bound to a complementary surface of a polymer support in a multipoint fashion. Biochem. Biophys. Acta. 485: 1-12; 1977.

6. Ottesen, M.; Svendsen, I. The subtilisins. In: Perlmann, G.E.; Lorand, L., eds. Methods in enzymology; v. 19. New York: Academic Press; 1970: 199-215.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

PLANT RESPONSES TO PETROCHEMICAL WASTES

Robert W. Duell and Fred E. Katz
New Jersey Agricultural Experiment Station
Rutgers, The State University of New Jersey
New Brunswick, NJ 08903

ABSTRACT

Petroleum products occasionally contaminate soil by spillage, while waste products of the petrochemical industry are regularly applied to designated sites called landfarms for land treatment or biodegradation by soil microorganisms. Vegetation is generally not employed in remediation of such contamination. In this research, vascular plants were sought which (1) might be used as bioassay, or indicator plants that might serve to identify surface contamination and (2) which plants would be tolerant of petrochemical waste contaminated soil, and thus serve to vegetate closed landfarm sites.

A procedure based on emergence of seedlings in contact with mixtures of diesel fuel and vermiculite was developed. In as little as 4 (and up to 7) days in a controlled environment germinator, 'Bison' ryegrass reacted predictably to increments ranging from 2.5 to 40% diesel fuel to vermiculite, v/v.

Various plant species grew in diesel fuel-contaminated media or in landfarm soil long contaminated with petrochemical wastes under conditions where moisture, nutrients, and air were provided by floatation of plants (rooted in contaminated medias) in styrofoam flats in hydroponic solution.

In landfarm fields where applications had ceased, soils were hydrophobic, saline, and high in pH. The latter values decreased with rainfall and irrigation. Vigorous grasses such as ryegrass started readily but failed to overwinter. Various fine fescues developed slowly but persisted better. Additions of composted sewage-sludge ameliorated adverse soil conditions and aided seedling establishment.

INTRODUCTION

Land treatment involves the periodic application and incorporation of wastes to, and in, soil. Petroleum industries have found this method of disposal to be cost effective when properly executed and EPA concurs that this method can be environmentally sound (Annon 1985). Such operations are described and compared with land treatment of other wastes in publications of the American

Petroleum Institute (Annon 1983, 1985).

Interactions of petrochemicals with terrestrial vascular plants have not been widely published. Perhaps the most extensive studies related are those conducted at the University of Alberta, Canada. Peaty soils that were contaminated by a single event with crude oil were revegetated most successfully by grasses (McGill and Nyborg, 1975). They also pointed out the advantages of legumes that would fix atmospheric nitrogen and thus not compete with the oil-degrading microorganisms for that essential nutrient element. Plant types most susceptible to oil-contaminated soil generally included seedlings, annuals, plants with large leaf surfaces or shallow root systems, as well as mosses and lichens (McGill et al, 1981).

In addition to accidental spills, problems of management and eventual closure of landfarms also confront the petroleum industry. Here, in designated areas, the oily wastes from tank bottoms and separator systems are spread periodically and tilled frequently to accelerate biodegradation of the petroleum fractions by the native microorganisms in the soil which use these hydrocarbons as an energy substrate.

Bartha (1979) surveyed various factors affecting microbial degradation of oil in landfarming soils. He reported a consensus in the literature that microbial degradation of oil was enhanced by aeration and fertilization, particularly with N and P when temperature and moisture regimes were favorable for bacterial activity.

Brown (1982) employed annual ryegrass (cultivar not stated) to measure the rate at which oily sludges were degraded. Others used organisms including earthworms and Daphnia, as bioassays to measure oil contents of various soils and oil-contaminated water. No extensive studies were found in the literature that related to the reaction of vascular plants, either sensitive to or tolerant of petrochemical contamination of soils.

PURPOSE

The petroleum industries are succeeding in reducing the oil fraction remaining in these wastes and certain landfarms are slated for closure. The question then arises as to the most appropriate means of vegetating these areas so that they will be less environmentally objectionable and more aesthetically acceptable.

Our hypothesis is that: certain plants will be very sensitive to petrochemical contamination of soil and others will be quite tolerant. The former would serve as indicator or bioassay plants, and the latter would be candidates for the vegetative cover of areas of soil contaminated with petrochemicals, either as spills or disposed as in landfarming operations.

APPROACH

Bioassay, or indicator plants, should respond, preferably quickly, to the target substance. Hence, germination trials in controlled environment chambers were replicated in media of various petrochemicals of known and reproducible materials or as-found in various landfarms of petroleum industries.

Successful plant species are then potential candidates for replicated growth-tests in styrofoam flats containing media similar to that described above. The flats float in complete nutrient solutions which are regulated to supply favorable regimes of nutrients, water, and air to all entries (typically 72 plants per flat). Several petrochemicals can be tested simultaneously in the same flat or adjacent flats in the same hydroponic pool without cross-contamination by the oil substrates.

Plants successfully coping with petrochemicals at this stage are candidates for long-term growth studies in replicated plots on closed landfarm sites. Retardation and growth abnormalities are noted as indicator reactions.

Problems other than petrochemical phytotoxicity were identified. These relate to the practical application of the fruits of this research to industrial interests.

Materials and Method, First Stage Bioassay

Seeds of numerous cultivars and species of grasses, legumes, flowers, and vegetables were tested in 3 replicates of 50 seeds each in 10 cm. diameter disposable petri dishes containing #3 grade vermiculite mixed with zero to 50% v/v of diesel fuel or petrochemical waste. Diesel fuel was used initially because it is universally available and a more uniform constituent than tank bottoms, bunker wastes, etc. Seeds were evenly distributed over 15 ml of the test or check mixtures, covered with an additional 15 ml of the same mixture and wet with 10 ml of water containing 0.25% v/v non-ionic wetting agent. Petri dishes were placed in a 100% relative humidity chamber with 12-hr light and dark periods at 26 and 20C, respectively.

Emergence counts were made at 4 and 7 day stages. Seedlings were scanned with magnifying lenses for abnormal reactions, lesions, and chlorosis.

Similar trials were conducted with petrochemically contaminated soils from various landfarms instead of mixtures of diesel and vermiculite. Gypsum was added at 1g/454g soil leached or 2g/454g and leached repeatedly. A non-ionic surfactant was added at 0.5% v/v to the 1L/900g of such soil of leaching water as indicated.

Several plant species initiated differential seedling growth at 4 days after seeding and sustained such at 7 days and beyond at rates of up to 50% on vermiculite (Table 1). This contrasts with the view of Overcash and Pal (1979) who wrote that oil concentrations over 4% may inhibit germination of annual grass.

RESULTS

Of the numerous grasses, legumes and other dicotyledonous plants that have undergone germination trials in contact with various petrochemicals, one cultivar of perennial ryegrass (*Lolium perenne*, L.) 'Bison' has consistently produced statistically significant differences in germination rates in as little as four days, in the presence of rates of diesel fuel as might be encountered in soils.

Cultivars of three species were consistently vigorous and responsive to petrochemicals used in these trials, and only they will be reported here. The results of emergence counts at both 4 and 7 days are shown in Table 1. Both Bison perennial ryegrass and 'Green Globe' turnip were significantly impaired by the first increment if diesel fuel at 7 days. These data were repeatable in a subsequent trial, hence Bison ryegrass is recommended as a bioassay species under the above circumstances.

Similar trials were conducted using petrochemically contaminated landfarm soils. All samples of such, thus far analyzed, proved to be saline and generally alkaline. These attributes probably derive from the disposal of alkylation sludge generated in the refining process (Annon 1985). Table 2 illustrates these characteristics (see conductivity and pH). The sample described as"acid field" was taken following a rainy period; subsequent sampling, after dry weather, revealed high pH values, comparable to the others. The addition of gypsum, with leaching, did reduce conductivity consistently, but also generally reduced germination of three bioassay species, as shown in Table 3. While landfarm samples differed in terms of these bioassays, the confounding factors of salinity and alkalinity are apparent, and may be more limiting to plant development than the oil contents of samples taken from closed landfarms.

When these same landfarm soils were treated with a non-ionic wetting agent prior to each of several leachings (with and without gypsum at 2g/454g soil), emergence in petri dishes was generally enhanced, as shown in Table 4. Specifically, emergence at 4 days for Bison ryegrass was improved in 4 of 5 treatments that received gypsum and had been leached. The exception was landfarm soil #2 where the difference was not statistically improved in soil numbers 3, 4, and 5. However, in sample #1, the gypsum treatment reduced emergence by 38%. Saranac had statistically significant reductions in leached soils 1 and 2, but showed improved emergence over the next three entries of soils leached with gypsum. Saranac was by far the best overall performer in this test where the salinity, alkalinity, and hydrophobicity of landfarm soils were involved.

Bison, however, was not the best performer in the secondary stage testing in greenhouse growth trials. Grasses such as weeping lovegrass (*Eragrostis curvula*), 'Atlantic' coastal panicgrass (*Panicum amarum* subsp. *amarulum*), and 'Midland' bermudagrass (*Cynodon dactylon*) have made better growth subsequent to establishment. This, of course, is important to revegetation efforts.

Intermediate Growth Trials

A series of trials was conducted to screen additional species and cultivars of vascular plants for potential as plants tolerant to petrochemicals and landfarm soil conditions. Commercially available styrofoam flats designed to contain plants in solid growing media were floated in complete nutrient solution in the relative stability and uniformity of a greenhouse.

MATERIALS AND METHODS

Rectangular styrofoam flats

contained 72 individual cells 5x5x5 cm in a 6x12 cell-pattern. Individual cells are 4 sided inverted pyramids with truncated apices leaving a 1 cm square hole where roots may emerge. Emerging roots were pruned frequently. These holes were plugged with filter floss to insure containment of the petrochemically-contaminated soil. Removing flats from the hydroponic solution each evening allowed for drainage and aeration, while replacement each morning assured ample and uniform moisture and nutrient supply to test plants. Hydroponic solutions in which the flats floated were formulated to provide all essential nutrients at 1/2 the strength of solutions recommended for periodic fertilization. The solutions were changed weekly to avoid salt build-ups.

Table 1. Percent of emergence of seedlings in contact with differing concentrations of diesel fuel.

	% emergence at 4 days		
% Diesel (v/v)	% Bison Ryegrass	% Green Globe Turnip	% Saranac Alfalfa
0	40.5 A[1]	66.0 A	17.0 A
2.5	3.0 B	53.5 B	14.0 AB
5.0	1.0 B	41.5 C	13.5 BC
10.0	.0 B	28.5 D	11.0 BC
20.0	.0 B	15.5 E	8.0 CD
40.0	.0 B	2.0 F	4.0 DE
50.0	.0 B	.5 F	1.5 E
	% emergence at 7 days		
0	73.0 A	86.5 A	60.0 A
2.5	51.0 B	85.5 A	42.0 B
5.0	48.5 B	78.5 A	39.5 B
10.0	32.5 C	65.5 B	38.5 BC
20.0	14.5 D	58.7 B	30.5 C
40.0	.0 E	22.5 C	9.0 D
50.0	.0 E	17.5 C	8.5 D

[1] Values with different letters in a column are significantly different at the 5% level of probability (Duncan's Multiple Range Test).

Five landfarm soils, two increments of #2 diesel on vermiculite fuel and four waste sludges mixed at 10% v/v with Freehold sandy loam were utilized for this trial. 'Pennant' ryegrass seedlings that had been started in a greenhouse single styrofoam flat.

Table 2. Chemical and physical characteristics of soils of the landfarming sites.

Soil media	pH	Bulk Density	Conductivity	Nutrient Status			
				Mg	P	K	Ca
		g/cm^3	mmhos/cm/s	lbs/A			
WESTERN SERIES							
#1	7.3	1.073	1.47	890+	32	73	6,995+
#2	7.4	1.073	1.89	890+	23	102	6,995+
#3	7.7	1.216	1.95	890+	<13	130	6,995+
#4	7.7	1.020	0.76	890+	<13	130	6,995+
#5	7.7	1.067	0.88	890+	<13	81	6,995+
EASTERN SERIES							
(s)	8.0	1.069	1.20	890+	<13	89	6,268
(NW)	8.3	1.151	1.65	890+	<13	111	6,288
(NE)	8.1	1.170	1.60	890+	<13	103	6,405
Acid Field	6.3	1.417	1.00	68	24	20	249

Samples were replicated six times in random fashion for a total of 72 entries. Flats were placed in nutrient baths on a day in/night out rotation.

Height data were taken at three weeks after planting. Plants were observed for recovery and growth. Plants were harvested after three months and dried at 70°C to constant weight. All data were analyzed using the ANOVA procedure provided through SAS. Means were compared using the Duncan Multiple Range Test.

Results and Discussion

Ryegrass plants established quickly and growth was generally good in all 12 treatments listed in Table 5. Numbers 5,8,10 and 11 achieved greater height than did the vermiculite check. Three of the above were sludges of petrochemical wastes, mixed at 10% v/v with Freehold sandy loam. The same materials had given poor results in germination Bioassay. The mean heights of "Tank Bottoms", two untreated samples from ES (eastern) landfarms and diesel fuel treatment vermiculite, were significantly less than check growing in uncontaminated vermiculite. Dry weight data are in general agreement with height data but do demonstrate a greater statistical spread.

The relatively good performance of transplanted seedlings, as compared with emergence data shown earlier, attests to the sensitivity of the early stage of plant development to such petrochemicals as tested here. Conversely, the good performance of seedlings such as Pennant ryegrass in prolonged contact with petrochemicals illustrates a high degree of tolerance of developed plants to such "toxic waste".

Table 3. Soil characteristics and emergence at 4 days of 3 plant species in petrochemically contaminated soils with gypsum added at 2g/454g, and without gypsum.

Landfarm soil identity & Treatment	Conductivity (mmhos/cm/5) soil/H_2O 2/1	pH (soil/H_2O=1/1)	Bioassy species: Bison Ryegrass	Green Globe Turnip	Saranac Alfalfa
			% emergence		
Check			37.5 b[1]	63.5 a	71.0 a
Western #5 (1	0.80	7.5	48.5 a	50.5 b	67.0 a
(1+Gypsum	0.70	7.6	2.0 e	8.0 def	15.0 ef
Eastern S (2	1.90	8.1	17.0 cd	6.0 efg	26.0 cd
(2+Gypsum	0.85	8.0	2.0 e	11.0 de	19.0 de
Eastern NW (3	1.60	8.2	21.5 c	4.5 fg	37.0 b
(3+Gypsum	0.70	8.1	10.0 d	12.5 d	29.5 bc
Eastern NE (4	1.40	8.0	22.0 c	21.0 c	33.5 bc
(4+Gypsum	1.00	7.9	2.5 e	5.5 efg	26.5 cd
Acid Field (5	1.05	6.0	2.0 e	0.0 g	11.5 df
(5+Gypsum	0.25	6.4	3.0 e	2.0 fg	8.0 f

1/ Duncan's multiple range; means within a column having different letters are significantly different at the 5% level.

Field Trials on Landfarming Sites

Having enlisted the cooperation of key personnel at local petroleum industry sites, we obtained not only samples of petrochemical wastes and soil contaminated with mixtures of these wastes over many years of using landfarm sites for disposal and biodegradation, but we also received cooperation in initiating field trials on three closed landfarm sites where no wastes had been applied in recent years. Two sites were being tilled on occasion, but no nutrients were being added. No perennial vegetation had volunteered, and only a few plants of the annual fall panicgrass (Panicum dichotomiflora) grew at the edges of the untilled field. Topography was not quite level, and it was later learned that a clay liner existed at depths of generally 1-2 feet.

MATERIALS AND METHODS

Chemical and physical characteristics of the above landfarming sites are given in the lower half of Table 2. These values for pH and conductivity have been found to fluctuate markedly; decreasing with wetting events, and increasing with drying. The code designation "acid field" was selected after initial testing during wet weather. Subsequent samples from that landfarm field, acquired during dry periods, were more commonly characterized by values of 8.2 for pH, and 1.35 for conductivity. Germinating seeds or seedlings may be injured by conductivity values of 0.5 to 0.8 in inorganic soils, and 1.0 to 1.5 in organic soils (Flannery, 1985).

Table 4. Effects of treatment with gypsum and leaching with non-ionic solution vs original landfarm soil, on characteristics and emergence of 3 species at 4 days.

			Bioassay species		
Soil #	Conductivity (mmhos/cm/5)	pH (soil/H_2O)=1/1	Bison Ryegrass	Green Globe Turnip	Saranac Alfalfa
			% emergence		
1 original	.44	7.9	4.5 df[1]	44.5 b	60.5 a
treated	.80	8.0	23.5 b	6.5 f	41.5 b
2 original	.75	8.2	20.0 bc	22.5 cd	64.5 a
treated	.40	8.2	16.0 bcd	18.5 de	43.5 b
3 original	1.90	8.1	1.0 f	0.0 f	18.0 f
treated	.85	8.0	9.5 def	19.5 cde	29.0 def
4 original	1.60	8.2	3.0 ef	4.0 f	28.0 ef
treated	.70	8.1	16.5 bcd	27.0 c	41.0 bcd
5 original	1.40	8.0	3.5 ef	3.0 f	37.5 bcde
treated	1.00	7.9	37.5 a	56.0 a	60.5 a

1/ Duncan's multiple range; means within a column having different letters are significantly different at the 5% level.

During drying conditions these 3 landfarms soils appear white with the salts that formed by the evaporation of soil moisture that rose to the surface by capillarity.

Sites selected for uniformity within these landfarms measured 45'x75,' except 45'x45' for the acid field. Three replicates at each site were each divided to test the effects of composted sewage sludge at the rate of 13 tons (6.5 tons dry matter) per acre, incorporated 4" deep by rototilling except composted leaf mulch was used for the acid field. Fertilizer was applied at 300 lb per acre of 10-20-10, gypsum at 2 tons per acre on the eastern series, and hydrated lime at 1 ton per acre on the acid field.

On September 5, 1985 in the eastern series, field S, 41 species and cultivars of grasses and legumes were sown by hand in random order in furrowed rows 18" apart into the prepared seedbed. The split-plot design entailed the added organic matter vs none as main plots and species as subplots. Landfarm field NW was similarly treated, but a non-replicated series of 120 grasses was sown. The acid field landfarm was similarly sown to 24 species and cultivars of grasses and 6 legumes on September 6, 1985. Seed-to-soil contact was assured by trodding the rows.

RESULTS AND DISCUSSION

Light rains following seeding did not suffice for significant emergence of sown species. Experimental areas were irrigated several times, and emergence of the

Table 5. Height and weight responses of Pennant ryegrass transplanted in petrochemically contaminated media.

Growth Media #	Description	Height, cm	* dry wt. gr.
1	Eastern "S" field, untreated	14.5 bcd	2.04 ab
2	Eastern "S" field, treated	14.7 abcd	2.15 ab
3	Eastern "NW" field, untreated	12.5 d	1.59 bcd
4	Eastern "NW" field, treated	11.8 d	.88 de
5	Acid field, treated	18.2 a	1.47 bcd
6	5% diesel, on vermiculite	13.3 cd	1.44 bcd
7	10% diesel, on vermiculite	17.3 ab	2.33 a
8	Freehold sandy loam + DAF Biox*	17.3 ab	2.33 a
9	Freehold sandy loam + tank bottom	12.6 d	.57 e
10	Freehold sandy loam + API sep. bottoms	16.8 abc	1.62 bc
11	Freehold sandy loam + Bunkers	17.8 ab	1.12 cde
12	Check = vermiculite	16.5 abc	2.04 ab

* #8-11 = petrochemical waste sludges, 10% v/v.

ryegrasses began. Other grasses and the legumes emerged more slowly, with the tall fescues, bromegrasses and reed canarygrasses ranking intermediate in seedling vigor, and the fine fescues, bentgrasses and legumes being slowest. None of the seedlings grew as well as was expected, and desiccation during winter and early spring caused severe losses to certain entries. The relatively fast-emerging ryegrasses had the poorest survival rates, and the much slower emerging and slower growing fine fescues generally survived best. The reed canarygrasses fared better than the tall fescues. At all 3 locations, seedling emergence, growth and survival were noticeably better in the organically amended half of each row. Surviving members, however, were too few to warrant numerical evaluation and statistical analyses. These trials were terminated. Plots were refertilized, organic matter reapplied to the same half of each replicate, the most promising grasses were resown, and irrigation frequencies were increased.
Emergence and early growth appeared superior to the previous year's experience and substantial data on suitability of grass species and cultivars, with and without compost amendments on three petrochemical landfarms are anticipated.

ACKNOWLEDGMENTS

This work was performed as a part of NJAES Project No. 15455, supported by the New Jersey Agricultural Experiment Station and NJIT. (D15455-2-87 Publication No.)

REFERENCES

1. Annon. 1983. Land Treatment Practices in the Petroleum Industry Prepared for The American Petroleum Institute by Environmental Research & Technology, Inc. Concord, Mass.

2. Annon. 1985. Land Treatment. The American Petroleum Institute, Environmental Affairs Dept., Washington, D.C.

3. Bartha, R., and Dibble, J.T. 1979. Rehabilitation of Oil-Inundated Agricultural Land: A Case Histgory. Soil Science. Vol. 128, No.1.

4. Brown, K. W., Brawand, H., Thomas, J. C., and Evans, G. B. 1982. Impact of Simulated Land Treatment with Oily Sludges on Ryegrass Emergence and Yield. Agronomy Journal. 74:257-261.

5. Brown, K. E. and L. E. Deual. 1982. An Evaluation of Subsurface Conditions at Refinery Landfarm Sites. Texas A & M. Prepared for the American Petroleum Institute and the Environmental Protection Agency Grant No. CR 807868. Original not seen.

6. Flannery, R. L., 1985. Soils Sheet #15, N. J. Ag. Expt. Stn.

7. McGill, W. B., and Nyborg, M. 1975. Reclamation of Wet Forest Soils Subjected to Oil Spills. Publication No. 6-75-1. Alberta Institute of Pedology. University of Alberta, Edmonton.

8. McGill, W. B., Rowell, M. J., and Westlake, D.W.S. 1981. Biochemistry, ecology and microbiology of petroleum components in soil. In: Soil Biochemistry (E. A. Paul and J. N. Ladd, eds.) Vol. 5, pp. 229-296. Marcel Dekker, New York.

9. Overcash, M. R. and D. Pal. 1979. Design of Land Treatment Systems for Industrial Wastes - Theory and Practice. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

STIMULATED IN SITU BIODEGRADATION OF AROMATIC HYDROCARBONS

Dr.-Ing. Peter Geldner
Associate Consultant Engineer
Karlsruhe, Federal Republic of Germany

ABSTRACT

A critical review of a closed remedial action applying in situ biodegradation at a contaminated site in the Upper Rhine Graben is presented. The practical solution finally accomplished to remedy an area of approximately 5,000 qm of soil and groundwater contaminated by benzene and other aromatics was based on the following approach characteristics:

1. Establishment and control of an artificial groundwater flow circuit by injection and extraction wells.
2. Stimulation of naturally existing microbial degradation by adding nitrate and essential nutrients to the injected water.
3. Striping and filtering the extracted water before reinjection.

Approximately 20 to 30 tons of hydrocarbons were degraded.

In this paper, further details of the case history is given and the attempt is made to derive first generalized criteria for the applicability of the method. Generalisation is discussed considering the strong role of individual site conditions, such as the geological structure and the natural microbiological capability of the soil and groundwater. As a result of the analysis, individual test programs, partly performed on a semi- field scale, and enforced permanent special supervision appear to be necessary presumptions for a successful implementation of the approach.

INTRODUCTION

Among remedial methods which destroy hazardous wastes rather than contain them, in situ biodegradation has been proposed as a preferable method. The attention the method has received may be caused by the fact that it does not demand intensive long-term controls over many years as is necessary for depositing or containing hazardous materials /1/. However, few field sites are known where the method has been sucessfully applied, at

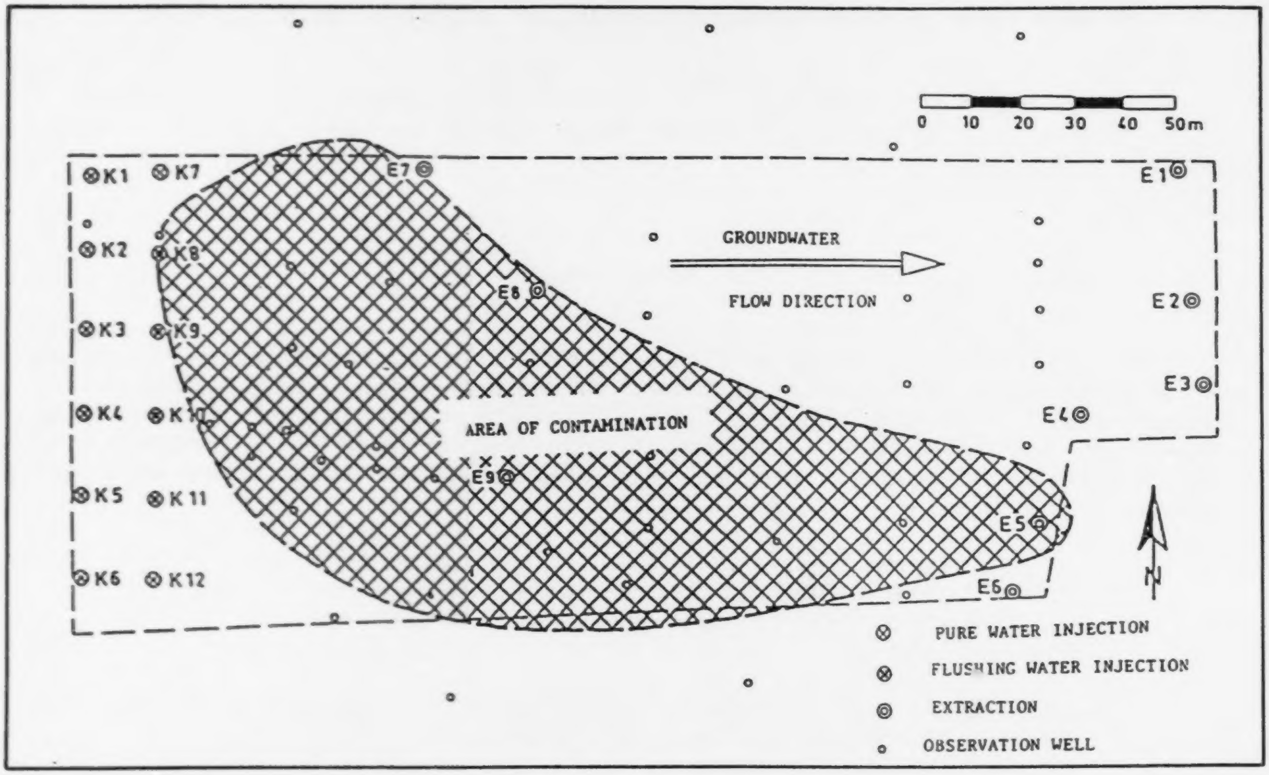

0 10 20 30 40 50m
K1
K7
E7
E1
K2
K8
GROUNDWATER
FLOW DIRECTION
E8
E2
K3
K9
E3
K4
K10
AREA OF CONTAMINATION
E4
E9
K5
K11
E5
K6
K12
E6
N
PURE WATER INJECTION
FLUSHING WATER INJECTION
EXTRACTION
OBSERVATION WELL

Fig. 1 Plan of the site and estimated extension of contamination

least little practical knowledge is available todate. This paper reports the engineering application of stimulated biodegradation in the subsurface environment of a former gas production site. From the engineering point of view, the stimulation of biodegradative processes in the field requires exceptional organisational und technological management. In order to guarantee high-level operational flexibility, which is absolutely necessary, the most important requirement is an efficient interdisciplinary team cooperation. The project was a cooperative effort among Björnsen Consultant Engineers (BCE), Koblenz), Engler Bunte Institute(EBI), The University of Karlsruhe, and the Federal Environmental Agency (UBA), Berlin/2/4/5/.

DESCRIPTION OF THE PROBLEM

The contamination occurred in a shallow aquifer of the Upper Rhine Graben. The site is a former gas-production facility near a medium-sized city. Over many years hydrocarbons of a gas cracking installation had seeped into the ground. Today, the exact circumstances cannot be redefined. The components of the contamination were ordinary fuel oil, forming the major part, and the aromatic hydrocarbons benzene, xylene, toluene, naphtalene und styrene.

As a preceeding measure oil in phase had been pumped out of the ground over three years, so that the actual remaining contamination was most likely limited to the residual saturation of the pore volume. Soil samples contained oil of approximately 1 % of the pore volume. The estimated total contaminated area is shown in Fig.1. The exact amount of both aliphatics and aromatics was unknown. The aromatics were considered the actual danger potential and increased aromatic concentrations were measured in the groundwater upstream of a municipal waterwork. Hydrocarbons in solution had indeed proceeded downstream from the site, and contamination of private irrigation wells had already occurred.

The Upper Rhine Graben aquifer is a sedimentary mainly quarternary formation. Its dominant characteristic is an irregularly layered structure. Sand and gravel layers of variable thickness and horizontal extension are seperated by clay and silt lenses. In the area of the contaminated site, there is a distinct layer of approximately 10 meters thickness ranging from coarse gravel-sand to fine sand. Peat layers of less than 10 cm were identified from core samples. The top layer is underlain by a very low permeable clay layer of 30 meters thickness or more.

At the end of the three year pumping period the saturated groundwater thickness above the impermeable base did not exceed 1 m and natural flow velocities were extremely low.

THE REMEDIAL METHOD

Several alternatives for the restoration of the contaminated site were considered. The second most favored method was containment of the site by a barrier ("tub" solution). The containment plan was turned down in favor of a combination of hydraulic flushing and induced in situ biodegradation. The solution was viewed as most promising concerning long-term effectiveness. The decision was based on the philosophy that containment would preserve the problem rather than solve it.

Remedial action at the site comprises two major steps:

(1) Hydraulic measures

(2) Microbiological supervision

An important requirement for the biological degradation is the establishment and control of an artificial large-scale subsurface flow system. A partial benefit of these hydraulic measures is the effect of flushing the contaminated soil. The injected water, after passage through the contaminated aquifer, is totally pumped out. The flushing products are separated by strip-aeration and sand-filtration to be ready for re-injection.

On the basis of the controlled groundwater flow as a subsurface transport system biodegration of the hydrocarbons is stimulated by enrichment of the injected water. The underlying biological process is produced by natural bacteria growth and artificial nitrate supply. Experience showed that essential nutrients such as phosphate and ammonium can have an important influence on the microbial activity. This should be avoided by the provision of appropriate substances at trace level concentrations. A moderate temperature increase of the injected water also accelerates the process.

PROCEDURE OF THE REMEDIAL METHOD

Clean-up Installation

A schematic representation of the on-site and subsurface facilities providing control of the water quality parameters is shown in Fig. 2. The chart reveals two separate circuits, the flushing circuit and the pure water injection of drinking water standard.

The latter was maintained throughout the remedial action providing a guarantee that contaminated flushing water would not enter the surrounding aquifer. The necessary water volume for the pure water injection was provided by a pumping well in all lower uncontaminated aquifer. In order to prevent clogging of the pure water injection wells, the water was stripped and filtered to separate iron and manganese constituents, also some methane.

A similar arrangement was used to strip the extracted water of the flushing circuit: The pumped water, containing flushed-out hydrocarbons and by-products of the biodegrada-

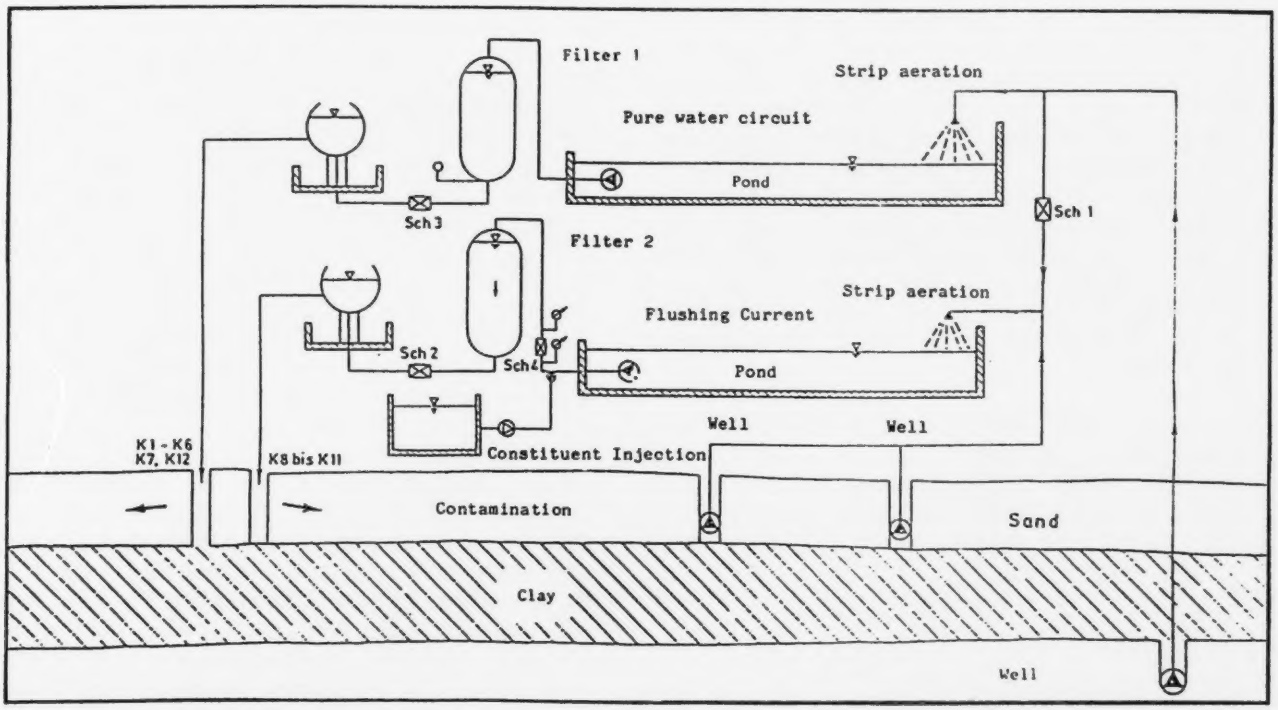

Filter 1
Strip aeration
Pure water circuit
Pond
Sch 3
Sch 1
Filter 2
Strip aeration
Flushing Current
Sch 2
Sch4
Pond
Well
Well
Constituent Injection
K1 - K6
K7, K12
K8 bis K11
Contamination
Sand
Clay
Well

Fig. 2 Scheme of the remedial facilities

tion, was aerated and filtered before being re-injected. Special installations allowed controlled doses of nutrients to be added into the flushing cycle. Also heating facilities were provided at this point of the circuit. The schematical cross-section between the injection and the extraction wells, demonstrates the principal function of the injected water penetrating the contaminated soil.

The pure water injection facilities consist of 8 gravel-filled wells, 9 meters deep and with a diameter of 0.6 meters. The flushing circuit has four wells of the same kind. The extraction wells are of similar specifications, however screened to the lowest 2 meters. Pure water can be injected at a rate of up to 20 l/sec and the average flow rate was 10 l/sec. The flushing-injection rate was 5 l/sec and the extracted water was adjusted to be always above this rate.

Flow and Constituent Transport

The build-up of an artificial groundwater flow system as a necessary means for the flushing of the contamination and as a transport medium was aided by a coupled flow and transport model. A major task of the model was to design the system in such a way that all injected water passing through contaminated soil or carrying artificially injected substances was indeed caught in the extraction wells. The authorities permit for the use of the unconventional method in the field required that both the injected nutrients and flushed products would be kept within a defined area, and that any artificial contamination of the surrounding aquifer caused by the operation would not occur at any time.

These requirements were met with the help of frequent calibration of a numerical model, regarding all incoming field data on a very short time basis. The model thus provided the information necessary for the consecutive steps of the operation. In reality, the provision of the necessary data demanded the presence of qualified personnel on site and a functioning communication between the site and the central computer facilities.

The flow model was calibrated during the "filling" period of the aquifer, that is during the rise of the water table to an average of 6 meters above the impermeable layer. This water thickness was sufficient to contain the polluted parts of the aquifer. The advance of the water front was measured by observing the groundwater heads in a dense grid of observation wells. Simultaneously data of water quality parameters such as temperature, electric conductivity and dissolved oxygen were taken. By the time steady state flow conditions were reached, the model was able to predict the effect of any changes of injection or withdrawal rates on the water table. An example of the calculated head distribution is shown in Fig. 3.

In order to predict the transport of constituents in the injection water, a transport model was calibrated by evaluating a number of tracer tests. Conservative tracers were used that were not influenced by possible chemical reactions in the polluted underground environment. Tracers were two different kinds of chloride and various flourescents. Nitrate was not injected in the aquifer until it was established that it would not leave the flushing circuit. To be on the conservative side, nitrate was treated as an non-reactive compound in the model calcula-

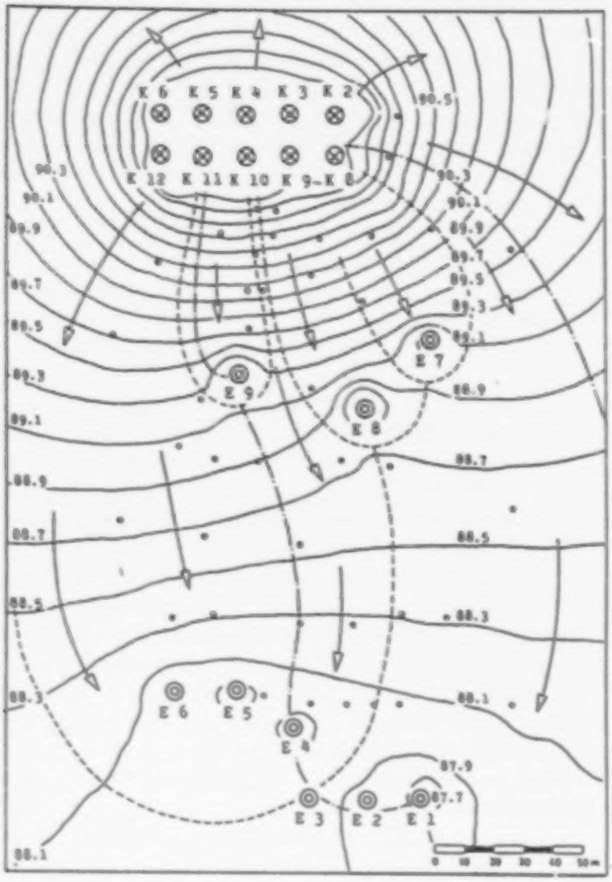


Fig. 3 Groundwater contour map

tions. Eventual measurements of the behavior of nitrate in the subsurface did, however, prove that this preventive assumption was never met due to intensive biochemical reactions.

Control of Biodegration Processes

The actual verification of the method in the field was preceeded by a series of microbiological tests in the laboratory. (For detailed results see also /2/). First results of the microbiological tests with wet soil samples, taken during drilling of observation wells at an early stage of the preliminary investigations, had proved the existence of microbial organisms in the subsurface environment, that were capable of degrading gasoline and benzene. Up to 5000 microbes with this ability were counted in one gram of soil. At the same time toxic constituents such as heavy metals, which may have prohibited microbial activity, could be shown to be absent.

Later, incubation experiments in the laboratory with water samples from the extraction wells gave more detailed insight into the degradation capability of the microbes in the water environment. The experiments over 7 and 17 days of breeding time, showed that aromatic hydrocarbons were clearly more intensively degraded than their aliphatic counterparts /2/. This means, that in the microbial environment present in the lab aromatic hydrocarbons were preferably "consumed" by the existing microbial population. Any general validity of this result cannot be claimed at this time. The same behavior was later confirmed in the field application.

Furthermore, there was a clear gradiation in the microbial acceptance of the different kinds of aromatics. Under incubation conditions, benzene was preferably degraded before xylene. The longest delay was observed for toluene.

On the basis of the results of these experiments, it appeared justified to implement the first step of an application in the field. After steady-state flow conditions had been reached, the injection water of the flushing circuit was enriched with low concentrations of dissolved nitrate. When measurements of nitrate in the observation wells indicated, that the oxygen donator had been accepted by the microbes, the injection concentration was gradually

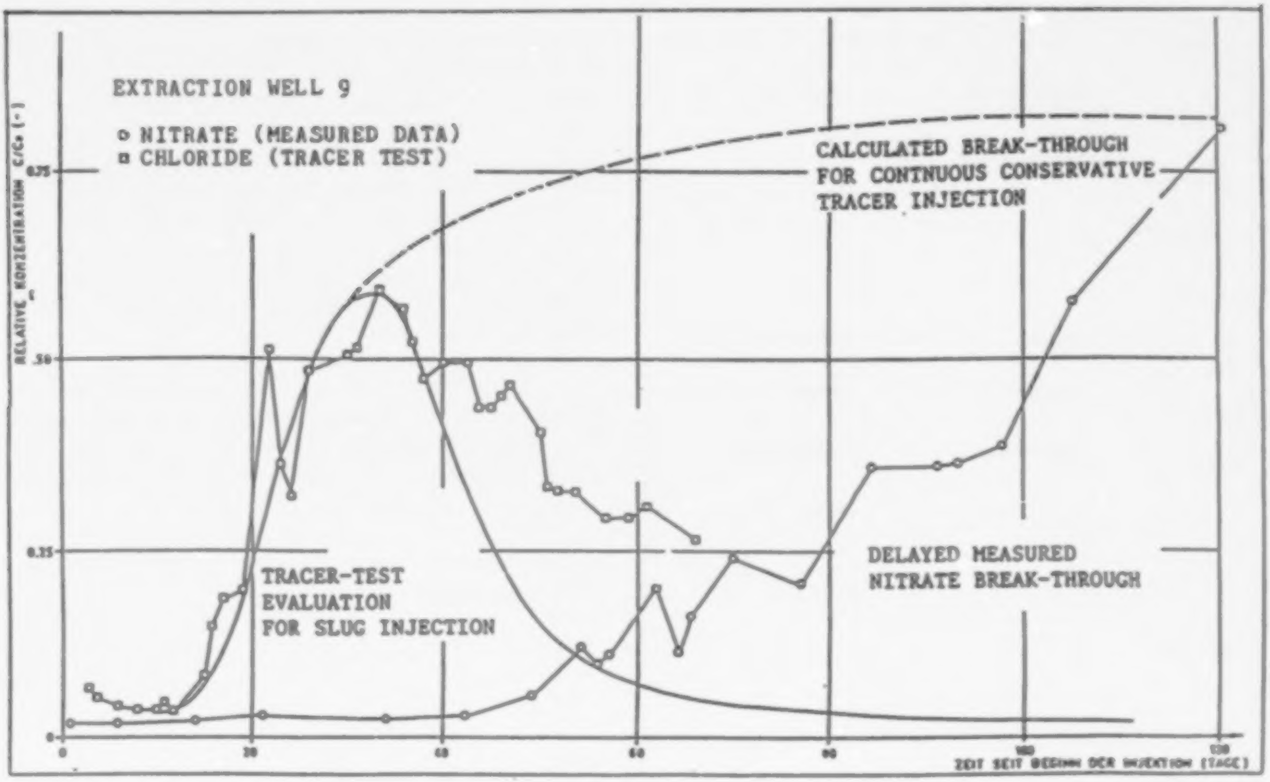


Fig. 4 Comparison of calculated conservative tracer transport and measured nitrate break-through curve

increased. Maximum values were up to 500 mg/l of nitrate and average injection concentration values ranged from 300 to 400 mg/l.

The observation of the nitrate concentration in the extraction wells was used to adjust the injected concentrations. They were reduced as soon as the nitrate level in the extraction went up, indicating that the degradation capacity of the system was reached.

The nitrate consumption could be shown by comparison of the break-through curves of a conservative (non-reactive) tracer calculated in the calibrated transport model and the measured break-through curves of nitrate /4/5/. In Fig. 4 an example of this comparison is shown. It is clearly recognized, that the calculated tracer break-through was much earlier than its measured counterpart. While this comparison for single well observations may still be affected by some random discrepancies due to the random structure of the aquifer, the calculations of concentrations in the extraction wells were sufficiently reliable. In fact, the nitrate concentrations in the extraction wells have never reached the injection concentration, although the total water

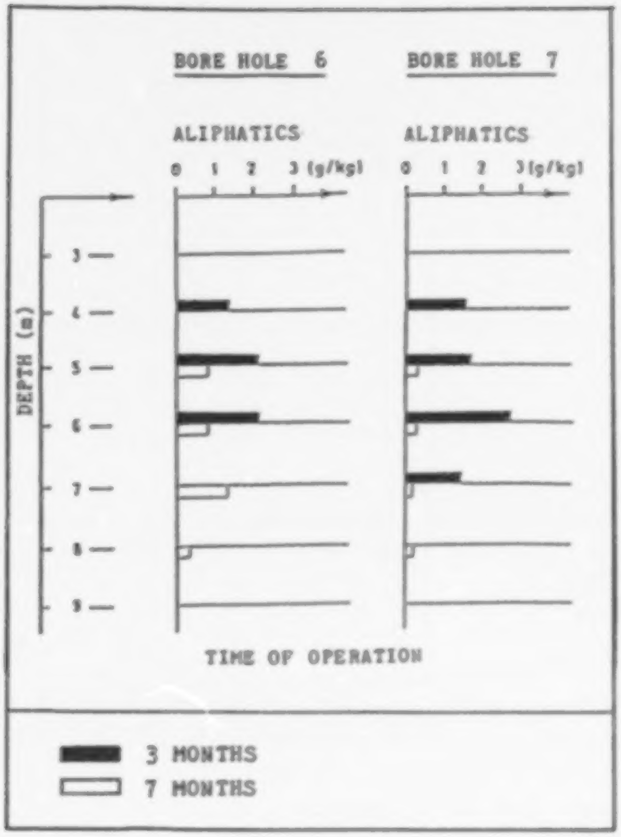


Fig. 5 Measured hydrocarbons in soil samples from different depths

volume in the aquifer between these wells had been exchanged many times during the on-going action. Microbial activity was also indicated by measurements of intermediate products of the degradation process in samples of the extracted water.

An important control of the effectiveness of the process was achieved by the analysis of randomly spaced borehole samples, which were taken over a time distance of 4 months. As shown in Fig. 5, the measurements indicate significant differences in hydrocarbon concentrations. It appears worthwhile mentioning that aromatic hydrocarbons had been degraded in the whole area of contamination, so that a major goal of the remedial action was achieved by 3 months. Due to the smaller degradibility of aliphatics, as already indicated by the results of the laboratory experiments, the aliphatics appear to respond to treatment slower than the aromatics.

In Fig. 6, the mean decay of hydrocarbon concentrations measured in the extraction well E 7,is plotted separately for aliphatics and

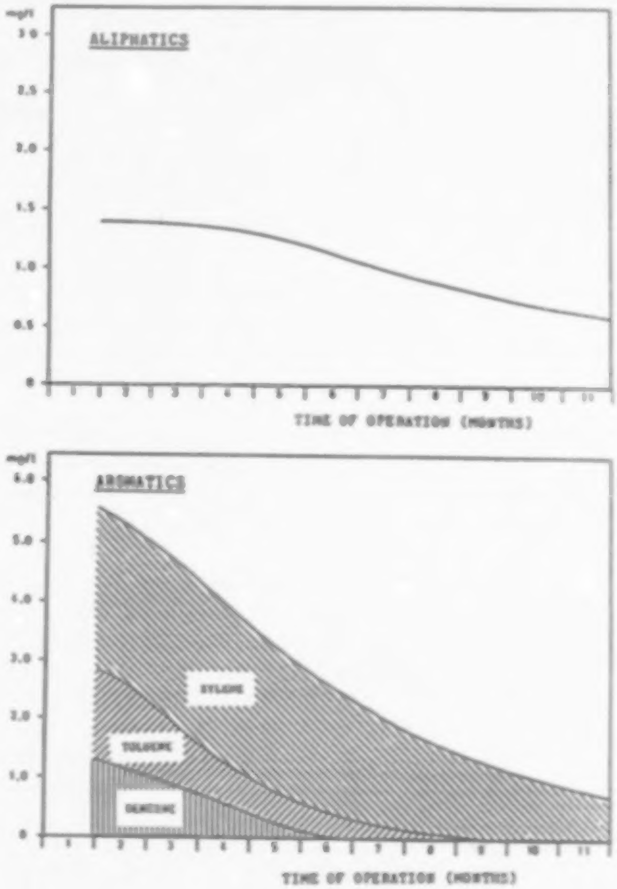


Fig. 6 Decay of hydrocarbon concentrations in extraction well No. E7

the different aromatic compounds. After two months, the aliphatics were reduced to about one third of the initial concentration. As indicated by the prelimnary laboratory experiments, also in the field, the aromatics were reduced sequentially. Benzene was followed by toluene, whereas, xylene was obviously last to be eliminated.

The described case-history shows that in situ biodegradation is not yet a standardized engineering method. Consequently a lot of development work had to be done in the project, so that an economic classification in terms of costs per cubic meter of remediated soil cannot reasonably be given. However, the following factors may provide some idea of the effort to be considered in planning a remedial action applying in situ biodegradation:

(1) Site investigations to estimate the extension of the contamination and evaluate principle flow and transport conditions in the subsurface

(2) Test of biodegradability of the contaminated soil (sampling, laboratory tests, choice of nutrients)

(3) Installation of piping and purification facilities for injection water and contaminated extraction water (dependent on the available local water supply and the kind of contamination)

(4) Establishment and sustaining of artificial flow conditions for possibly months or years (injection, pumping and monitoring facilities, tracer tests, model-calculations)

(5) Injection of nutrients possibly in large amounts and thermal energy supply

(6) Monitoring of control parameters of the injected and extracted water, dosage control and maintenance of purification facilities

(7) Efficiency control by parasampling and analysis of indicative parameters on-site and in the laboratory (predominantly during the operation period)

In the light of these necessary efforts, it would be misleading to derive economic considerations from laboratory results. Dependent upon the individual site conditions, costs for the application of in situ biodegradation may well reach a similar level as known for other more technologically oriented methods. Optimal applications from the economic point of view, seem to exist at sites with relatively low contaminant concentrations possibly due to intensive contaminant transport.

DISCUSSION

Based on a variety of measurements, the remedial action described has been accepted by the responsible environmental authorities as successful in the sense that the contamination is reduced down to a level that does not exert any harm to human health or violate environmental interests. In particular it has been accepted that all aromatic hydrocarbons are totally remediated, so that the predominant goal to abolish potential danger of carcinogenic substances in the ground is achieved. The applied method was successful at this individual site and very valuable experience could be made. However, a generalization of the method cannot be claimed at present. Further specialized investigations are necessary to clarify a number of open questions, should the approach be recommended as a general method.

Any further application should be aware that engineering modifications or alternatives may be needed, and that a good deal of development has to be done in any new project due to the lack of general knowledge. Future investigations can be envisioned on the grounds of the experiences made at this individual site as to concern the following fields:

(1) In-depth clarification of the underlying biochemical and hydraulic processes

(2) Improvement of the technical scheme

(3) Formulation of standards and limits to define the precise goal of remedial actions by biodegradation

Investigations of the biochemical processes in the soil should concentrate on the evaluation of typical microbial communities present in frequently occurring contaminations. The special nature of the problem seems to make it necessary to combine laboratory and field studies. It appears worthwhile to try to perform also field experiments on a scale that exceeds ordinary laboratory set-ups. A major task of such investigations would be to evaluate the time-scale of the biodegradative processes and possible accelerating factors. Special emphasis should be given to possible toxicity of intermediate metabolic products.

Further research needs exist in the understanding of microscopic transport processes in the pore volume of the aquifer with regard to different types of soils or settings. The influence of variable permeability and pore size distributions on the intensity of biodegradative processes is practically unknown. Partial layering of the aquifer may also limit the efficiency of the process. Stratification due to density differences may in certain situations reduce access of the nutrients to the biodegradable contamination and thus slowdown the process. Experience onsite has shown that certain improvements of the technical set-up may increase the efficiency of the measure. It would, for instance, be promising in shallow aquifers to use infiltration canals instead of arrays of injection wells. A major advantage would be that clogging of the screens could be avoided and that the much better accessibility would allow easy cleaning of clogged bed areas. It would even appear more economical in many cases, especially since the costs for piping facilities would be avoided. Another suggestion to improve accessibility of the soil for infiltrating nutrient enriched water is area flooding. If the conditions on site allow such an infiltration system, the unsaturated zone and the upper parts of the aquifer could be much better provided with the nutrient substrate.

Since biodegradative processes are based on fairly large time scales and finally reach exponential decay characteristics, it would be of practical importance to have adequate standards defining a realistic duration of the remedial action. Furthermore, standardized instructions of efficiency control measurements would be helpful in determining total time and material efforts needed in a certain situation. Special regard will have to be given to the formulation of such standards, in terms of spatial variability allowance for control measurements of remedied concentrations of individual contaminants. Very similar needs would be met by technical recommendations concerning observations of long-term effectiveness of a biodegradative remedial action.

REFERENCES

/1/ Smith, M.A. (ed.), 1985, Contaminated Land-Reclamation and Treatment, NATO-Challenges of Modern Society, Vol.8, Plemm Press, N.Y. and London.

/2/ Battermann, G. and Werner, P., 1984, Beseitigung einer Untergrundkontamination mit Kohlenwasserstoffen durch mikrobiellen Abbau, gwf/Wasser-Abwasser (125).

/3/ Nehrkorn, A., 1986, Bedeutung biologisches Vorgänge im Grundwasser; In: Wasser-unser Nutzen, unsere Sorge, DVWK-Schriften 78.

/4/ Geldner, P., 1986, Simulationsmodelle zur Ausbreitung von Schadstoffen im Untergrund; In: DVGW-Schriftenreihe Wasser Nr.45.

/5/ Zipfel, K. und Geldner, P., 1983, Veränderung der Grundwasserqualität bei der Wassergewinnung etc., Forschungsberichte UBA-10202303/12.

Disclaimer

The work in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

BACTERIAL TREATMENT OF PCB-CONTAMINATED SOILS: PROSPECTS FOR THE APPLICATION OF RECOMBINANT DNA TECHNOLOGY

Ronald Unterman, Frank J. Mondello, Michael J. Brennan, Ronald E. Brooks,
David P. Mobley, John B. McDermott, and Charles C. Schwartz

General Electric, Corporate Research and Development
Schenectady, New York 12301

ABSTRACT

We have assessed the efficacy of several natural bacterial isolates for decontaminating PCB-laden soil. Initial studies using Aroclor-spiked laboratory soil demonstrated extensive biodegradation by Pseudomonas putida strain LB400. More recent studies have focused on actual PCB-contaminated soil from New York State containing 525 ppm of transformed Aroclor 1242 (similar in composition to Aroclor 1248). Under laboratory conditions, 50% of these PCBs were degraded in three days, whereas using experimental conditions more suitable to an in situ application of bacteria, 50% degradation was achieved in 15 weeks. We are currently making final preparations for conducting a PCB biodegradation field test. In parallel studies we have recently cloned from strain LB400 the genes which encode the first several enzymes in the pathway for PCB biodegradation. These recombinant bacteria now offer the opportunity for engineering an improved PCB-degrading organism (this strain improvement is currently under way). We describe herein possible approaches for studying the biodegradation of soil-bound PCBs by genetically-engineered bacteria.

INTRODUCTION

The polychlorinated biphenyls (PCBs) were widely used over the last half century for many industrial applications. Because of their accumulation in the environment and possible health effects we began a research program several years ago to investigate the bacterial degradation of PCBs (for a review of this subject see reference 1). We initially isolated over two dozen new bacterial strains capable of biodegrading PCBs. Our subsequent studies have concentrated on characterizing the biochemistry and genetics of PCB biodegradation in several of these microorganisms (2-7). In parallel to these studies, we expanded our research program to explore the possibility of using one or more of our natural bacterial isolates for the decontamination of PCB-laden soil. Corynebacterium sp. MB1, Alcaligenes eutrophus H850, and Pseudomonas putida LB400 had all been shown to have excellent PCB-degrading capabilities under laboratory assay conditions (4-7), however, little was known about their ability to oxidize PCBs adsor-

Preceding page blank

bed to soil. Our initial studies using sand as a model demonstrated that PCBs were biodegradable even when bound to a solid substrate. Recently we have been conducting biodegradation studies using PCB-laden soil containing either Aroclors or pure PCB congeners (8).

RESULTS AND DISCUSSION

Biodegradation of Soil-bound PCBs

After initial studies with PCBs added to clean soil (8) we began studies with actual PCB-contaminated soil from New York State. This soil was from the site of a former drag strip where PCB oils (Aroclor 1242) were used for dust control. The sample we obtained was analyzed and contains 525 ppm of a transformed Aroclor 1242. It is depleted in the di- and trichlorobiphenyls and therefore appears similar in composition to Aroclor 1248. Resting cell biodegradation studies using the dragstrip soil have shown substantial PCB biodegradation. Strain LB400 degraded 15% of the PCBs in one day and 51% in three days (8).

In preparation for a site test at the drag strip, we scaled up our laboratory experiments (5 kg dragstrip soil) and adopted experimental conditions more suitable to an *in situ* application of bacteria. Using these conditions (3-4% of the previous cell concentration, unwashed cells, less water, 8°C cooler (22°), no shaking, less aeration) PCB biodegradation was much slower than observed with the resting cell protocol.

Eventually this laboratory study did show significant PCB biodegradation, albeit in weeks rather than days. In an undisturbed soil sample (1 kg), inoculated three times weekly with LB400, 50% of the PCB in the topmost soil was biodegraded in 15 weeks (Figure 1, center). In parallel experiments, 5 kg of dragstrip soil were inoculated three times weekly with LB400, but then mixed after each application. After 23 weeks, the PCBs in this soil are 35% biodegraded at all depths (Figure 1 bottom). Although this sample shows less percent biodegradation than the unmixed soil experiment discussed above, it exhibits a much greater total amount of PCB destruction.

We conclude from these results that it should be possible to biologically degrade PCBs on contaminated soil in the environment with appropriate cell concentrations and environmental conditions. Our continuing studies are now focusing on experimental conditions that most closely model an actual site decontamination process and, as planned, an *in situ* environmental test. However, it is clear that it would be desirable to have faster degradation rates, less temperature dependence, and effective degradation at lower bacterial levels. These goals are potentially accessible by genetic engineering through the incorporation of gene constructs which would produce greater quantities of the required enzymes.

Isolation of the Genes for PCB Metabolism

As part of our investigations on bacterial PCB metabolism we have begun to examine the regulation and control of the enzymes involved in this process. The ability to isolate and manipulate the genes encoding these enzymes would greatly facilitate these studies and our attempts to maximize the PCB degradative competence of our organisms.

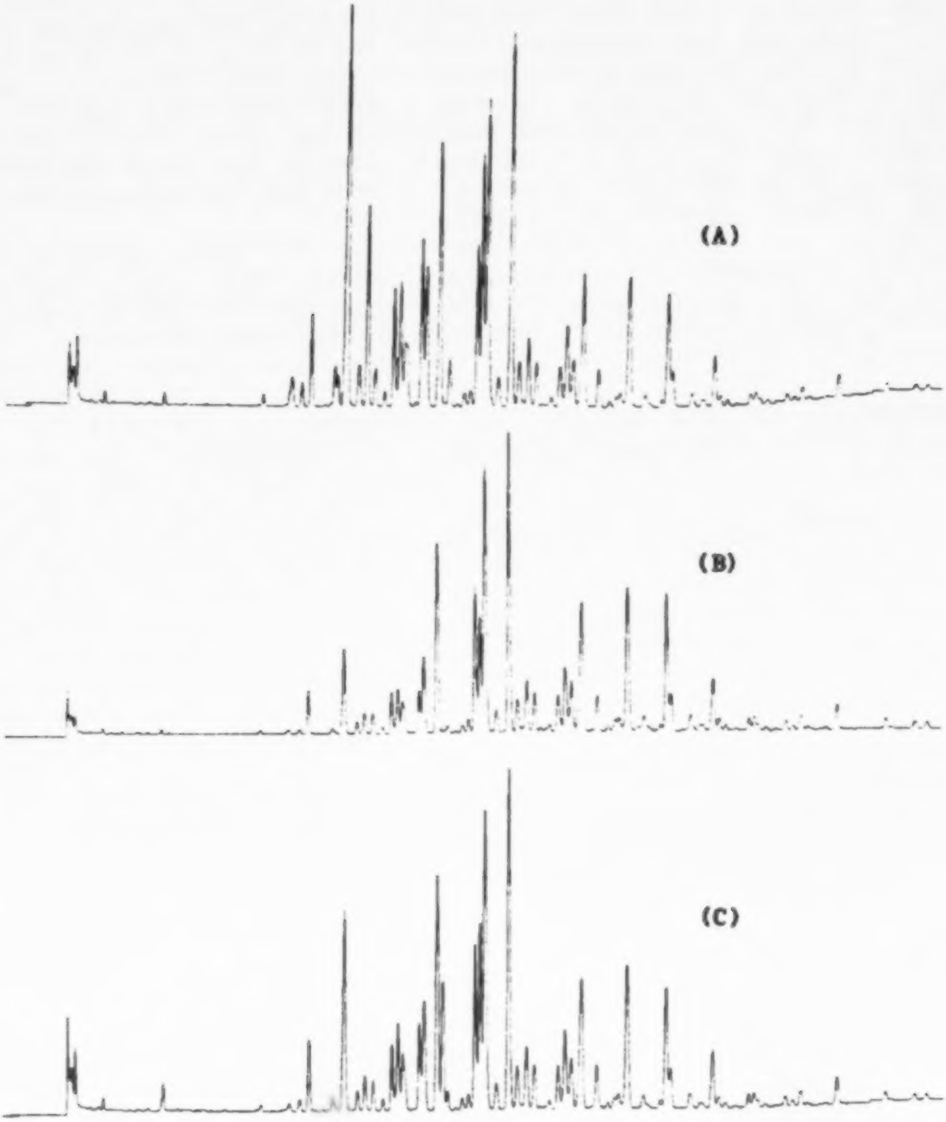


Figure 1. Gas chromatograms of biodegraded soil-bound PCB. (A) Buffer-dosed control, mixed; (B) Inoculated, unmixed, 15 weeks; and (C) Inoculated, mixed, 23 weeks.

A genomic library of *P. putida* LB400 was constructed and placed into an *Escherichia coli* host. From this library, recombinant strains that contained and expressed the genes for the PCB degradative enzymes of LB400 were isolated. Several of these *E. coli* strains have been found to possess all of the enzymes required to metabolize a variety of PCBs to their corresponding chlorobenzoic acids. This result conclusively demonstrates the presence of the four key enzymes of the PCB/biphenyl metabolic pathway (Figure 2).

Approaches for Biodegrading Soil-bound PCBs by Genetically Engineered Bacteria

We are now in a position to explore the potential of using genetically-engineered bacteria to biodegrade soil-bound PCBs by integrating our two previously independent lines of investigation: 1) the very promising model studies using *P. putida* LB400 to biodegrade PCBs on soil, and 2) the recent successful cloning of the PCB degradative genes from LB400. In the coming months our genetic research will include: (1) studies on the regulation of PCB/biphenyl degradation so that expression can be enhanced and controlled, (2) use of the LB400 gene clones to isolate and study the PCB/biphenyl genes from other organisms, and (3) combining of the genes from different organisms to facilitate the metabolism of PCBs and PCB intermediates.

Following completion of each of these three goals, we will have available new and/or improved recombinant DNA organisms. Therefore, one could begin to assess the activity of these novel strains of recombinant bacteria for degrading soil-bound PCBs. The approach would be similar to that used for our laboratory PCB/soil studies using native LB400 (as discussed above). Each new genetically-engineered bacterium could be assayed for its ability to degrade PCBs on both: 1) Aroclor 1242-spiked clean soil (500 ppm), and 2) Drag strip soil (525 ppm Aroclor 1248-like) using both resting cell and *in situ* protocols.

Specifically one could assay the soil PCB-degradative activity of:

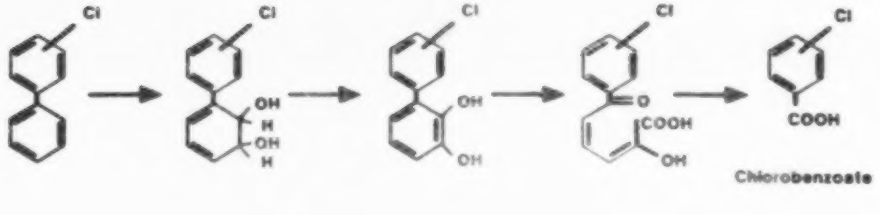


Figure 2. PCB metabolic pathway.

1. a first generation high expression engineered bacterium. This organism would be designed to synthesize higher levels of cloned LB400 PCB-degradative enzymes and may show increased rates of PCB biodegradation.

2. a possible second PCB-degrading recombinant strain whose PCB-degradative activity complements that of LB400. If this is achieved, then soil studies with this genetically engineered organism could be conducted using both pure as well as mixed cultures (with the LB400 derived strain). This may eventually lead to a superior mixed culture approach to PCB biodegradation (as discussed in reference 8).

3. a recombinant strain designed to combine from different organisms genes for the metabolism of PCBs and/or recalcitrant PCB metabolites. This organism might exhibit novel or improved PCB-degradative activity and would be an excellent candidate for assaying on PCBs bound to soil.

In summary, it will be important in the future to evaluate each new genetically-engineered PCB-degradative strain for its ability to degrade PCBs as actually found in the environment. This integration of genetic and soil studies is a logical and practical extension of important and promising research on PCB biodegradation. Thus, we are now in a position to exploit the potential of modern biotechnology for biodegrading environmental contaminants such as PCBs.

ACKNOWLEDGEMENTS

We would like to thank Robert Wagner for his expert GC analyses, and Carolyn Meyer and Marsha Berry for typing the manuscript.

This research was funded in part by the U.S. Environmental Protection Agency (contract #CR-812727-02-0), Dr. P.R. Sferra, project officer.

REFERENCES

1. Furukawa, K. (1982), "Microbial Degradation of Polychlorinated Biphenyls," pp. 33-57, Biodegradation and Detoxification of Environmental Pollutants, A.M. Chakrabarty (ed.), CRC Press, Inc., Boca Raton, FL.

2. Bedard, DL, Brennan, MJ and Unterman, R. (1984), "Bacterial Degradation of PCBs: Evidence of Distinct Pathways in *Corynebacterium* sp. MB1 and *Alcaligenes eutrophus* H850," pp. 4-101 to 4-118, Proc. 1983 PCB Seminar, Electric Power Research Institute, Palo Alto, CA, G. Addis and R. Komai (eds.).

3. Unterman, R., Bedard, DL, Bopp, LH, Brennan, MJ, Johnson, C. and Haberl, ML (1985), "Microbial Degradation of Polychlorinated Biphenyls," pp. 481-488, Proc. Intl. Conf. on New Frontiers for Hazardous Waste Management, U.S. Environmental Protection Agency, Cincinnati, OH.

4. Bedard, DL, Unterman, R., Bopp LH, Brennan, MJ, Haberl, ML and Johnson, C. (1986), "Rapid Assay for Screening and

Characterizing Microorganisms for the Ability to Degrade Polychlorinated Biphenyls," *Appl. Environ. Microbiol.* *51*, 761-768.

5. Bopp, LH (1986), "Degradation of Highly Chlorinated PCBs by *Pseudomonas* strain LB400," *J. Ind. Microbiol.* *1*, 23-29.

6. Bedard, DL, Wagner, RE, Brennan, MJ, Haberl, ML and Brown, JF (1987), "Extensive Degradation of Aroclors and Environmentally Transformed PCBs by *Alcaligenes eutrophus* H850," *Appl. Environ. Microbiol.* *53*, 1094-1102.

7. Bedard, DL, Haberl, ML, May, RJ and Brennan, MJ (1987), "Evidence for Novel Mechanisms of PCB Metabolism in *Alcaligenes eutrophus* H850," *Appl. Environ. Microbiol.* *53*, 1103-1112.

8. Unterman, R., Brennan, MJ, Brooks, RE and Johnson, C. (1987), "Biological Degradation of PCBs," *Proc. Intl. Conf. on Innovative Biol. Treatment of Toxic Wastewaters*, in press.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

SCREENING STUDY FOR ON-SITE BIOLOGICAL REMEDIATION OF SOILS CONTAMINATED BY COAL CONVERSION RESIDUALS AND BY-PRODUCTS

A. Brenner, R.L. Irvine, L.H. Ketchum, Jr. and C.F. Kulpa, Jr., P.O. Box G, University of Notre Dame, Notre Dame, IN 46556 and J.P. Moreau, Niagara Mohawk Power Corporation, 300 Erie Boulevard West, Syracuse, NY 13202

ABSTRACT

The purpose of this study was to investigate the feasibility of using the Sequencing Batch Reactor (SBR) as a key component in an on-site biological remediation program for the treatment of contaminated soil and leachates present at Niagara Mohawk Power Corporation's Harbor Point site in Utica, New York. Soil and leachate samples brought from this site were tested for biological activity. Plate counts and carbon evolution from soil respirometers verified significant activity of indigenous soil microorganisms. Laboratory-scale SBRs were tested using several operating strategies. The SBRs removed most of the soil and leachate constituents while producing "Specialized Bacteria" resistant to cyanide. Results from Chemical Oxygen Demand (COD) measurements and gas chromatograph analyses of selected target organics showed high removal efficiencies.

INTRODUCTION

Various residuals and byproducts of the coal carbonization process that were produced by two former gas manufacturing plants that were owned and operated from 1902 to the mid 1950's by one of Niagara Mohawk's predecessors, the Utica Gas and Electric Company, were disposed of at a 70 acre parcel known as Harbor Point. As a result, the soils and leachates at Harbor Point are contaminated with typical coal gasification materials such as polynuclear aromatic hydrocarbons (PNAs), phenols, coal tars and oils, purifier waste containing cyanides and sulfates, ash and other debris.

The purpose of this study was to investigate the potential of the Sequencing Batch Reactor (SBR) as a key component in an on-site remediation program for the Harbor Point site. The laboratory-scale SBR was to be integrated into an overall test system which included the biological degradation of hazardous organics found in leachates and soils and the production of "Specialized Bacteria" in the SBR for eventual application to the soils. This unique approach to soil decontamination, extends the innovative features of the SBR that were described by the United States Environmental Protection Agency (7,14), the National Science Foundation (2), and the U.S. Congressional Office of Technology Assessment (22).

The SBR has been shown to be a cost effective and energy efficient means for degrading hazardous wastes (10,11,13). It is uniquely suited for the selection and enrichment of the desired microbial population because of the ease with which a diverse array of operating strategies and selective pressures can be implemented (4,5,12,15). The convenience in operation stems from the time oriented nature of the process. Specifically, each tank in the SBR system is filled during a discrete period of time. During this period, organism selection can be controlled by manipulating the maximum growth rates of the microbes and by regulating the oxygen levels in the reactor (e.g., from anaerobic to aerobic). After a tank is filled, treatment continues as the SBR behaves as a batch reactor. During this period further selective pressures are applied by controlling the length of time the organisms are subjected to starvation conditions. After treatment, the microbes are allowed to settle and the clarified supernatant is drawn from the reactor.

During these quiescent periods, the opportunity for plasmid exchange and general enrichment of genetic information are enhanced. "Specialized Bacteria" developed in the SBR can be added to contaminated soils using well developed municipal sludge application technologies (23,25). Of these, surface application methods provide the best opportunity for maximizing the rate of soil detoxification. The results reported upon herein focus on SBR operation and performance and not on in-situ soil detoxification.

PURPOSE AND APPROACH

Experimental work of this study included two phases. Phase I initiated in July 1986 and continued through November 1986, was aimed at determining if the soils and leachates at the Harbor Point site can be treated biologically. This phase consisted of three independent tests which were: (1) Determination of chemical characteristics of the leachates; (2) Analysis of biological characteristics of the soils which included growth experiments and respirometer tests; and (3) Operation of two "initial screening" batch biological reactors being fed contaminated leachates and soils. These initial tests were the basis for a rather extensive phase II study which was initiated in November 1986 and continued through March 1987. During this phase, four laboratory scale SBR's were tested for biological degradation of the soil and leachate contaminants.

There have been several reports that bacteria present in sewage sludge degrade either phenols (21), PNAs (3), or cyanides (16). However, combination of all these substances in one stream requires a careful and innovative approach. This concept was applied in operating the laboratory SBR's. As a result, the reactors were operated with (1) either continuous or instantaneous feed modes in order to test the impact of shock loads; (2) with either completely aerobic or an anaerobic/aerobic sequence with a nitrate supplement in order to compare removal efficiencies with these operating strategies; and (3) with a carbon source (glucose) added in order to determine if cyanide removal was enhanced during denitrification.

Most of the chemical analyses of this study were conducted according to procedures described in "Standard Methods" (1). COD was determined by Dichromate Reflux Method (508C). Ammonia nitrogen was analyzed by the Nesslerization Method (417B), and nitrate and nitrite nitrogen by the Cadmium Reduction Method (Hach modification (8)). Total cyanide was determined by Method 412A.B.C.

Total bacterial counting analyses were performed by the Spread Plate Method (907B (1)) on Trypticase Soy Agar (TSA).

Gas chromatograph (GC) analyses were conducted according to procedures in the "Federal Register" (6). The GC used was a Varian 3700 with Vista 401 data processor. Three methods were used for detection of three compound groups typical to coal gasification wastes. In each method, specific compounds were selected as target compounds to be compared to standard solution data. The three methods and the selected target compounds were: (1) Purgeable Aromatics (Method 602) for Benzene, Toluene and Xylenes; (2) Phenols (Method 604) for Phenol; (3) Polynuclear Aromatic Hydrocarbons (Method 610) for Acenaphthene, Acenaphthylene and Naphthalene.

RESULTS

Leachate Chemical Characteristics. Three soil samples and one leachate sample were collected at the Harbor Point site on June 25, 1986. The soil samples were designated 1, 2, and 3 with soil 1 being the least contaminated and soil 3 the most contaminated. The leachate sample was collected at the soil 3 site. The leachates have a low pH of about 2.7, sufficient ammonia nitrogen and phosphate phosphorus to support biological growth, and less than 100 mg/l of soluble COD. As a result, biological treatment of the leachates alone may not be possible unless they are augmented by some other energy sources which will support the growth of an active biomass. As will be described and discussed later, leachates fed to the SBRs were supplemented with contaminated soils so as to promote bacterial growth, to develop a more diverse biological population, and to enhance the biological removal of target organics present in the leachates and soils. A glucose supplement was also tested in some reactors.

Bacterial Examination of the Soils. Growth experiments were conducted to characterize the organisms present in the soil and to determine if they were able to grow on the organic constituents, hazardous or non-hazardous. The growth potential of the organisms present in the soil samples were tested on Trypticase Soy Agar (TSA). This was done by adding a 2g soil sample to 100 ml of basal salts medium in a 250 ml flask and shaking at 28C for two weeks. Small aliquots removed from each soil flask on a regular basis were plated on TSA medium and the number of Colony Forming Units (CFU) produced counted. Results obtained for all three soils are plotted on Figure 1. As can be seen, soil 1 had the highest initial counts at about 4000 CFU/ml. The initial counts for soil 2 were 20 CFU/ml and for soil 3, 200 CFU/ml. This corresponds to approximately 200,000, 1000, and 10,000 CFU per g of soil, for soils 1, 2 and 3 respectively. Considering the fact that not all of the aerobic organisms present in the soil would be detected on the TSA medium and that none of the anaerobes would be measured by this procedure, these results indicate that a significant indigenous population is available at the Harbor Point site to assist in a biological remediation program if provided optimal growth conditions. Indeed, the aerobic, mixed environment established in the flasks did result in a 1000 fold increase in numbers of organisms in soils 1 and 3 and a 10,000 fold increase in soil 2. The die off of organisms at the end of the experiment in flasks containing soils 2 and 3 may have resulted from the exhaustion of readily usable carbon sources or from the accumulation of toxic organics leached from the soils during the course of the test.

A total of 29 bacteria were isolated from the soil growth flasks and cloned to purity. Of these 8 or 9 may be different strains of bacteria. These isolates were tested for their ability to grow on acenaphthene (0.01%), naphthalene (0.04%, and 0.1%) and phenol (0.01%, 0.1%, and 0.5%) as sole carbon sources. The controls were plates containing no carbon sources. Two of the isolates were capable of growing on 0.01% acenaphthene, five of the isolates on 0.04% naphthalene, and five on 0.01% phenol. Two of the colonies having distinct morphological characteristics on the plates were able to grow on all three carbon sources. No growth was observed in 0.1% naphthalene or on either 0.1% or 0.5% phenol.

Further evidence of the biological activity of the naturally occurring organisms at Harbor Point was obtained from the measurement of carbon dioxide evolution in soil respirometers. In these studies, 50g of each of the soils 1, 2 and 3, used in the growth studies described above, were placed in separate soil respirometers. Carbon dioxide evolution was measured by trapping in KOH and titration with acid. Results from these experiments are presented in Figure 2. From this figure it can be seen that soil 3, the most heavily contaminated soil, showed the lowest rates of CO_2 evolution. Soil 2 had an intermediate rate of evolution and soil 1 had the highest rate. All data points have been corrected with data from sterilized control soils. On day 27, inorganic nutrients (0.05g K_2HPO_4, 0.045g KH_2PO_4, 0.02g $(NH_4)_2SO_4$, and 0.0016 g $MgCl_2$) were added to the soils. No increase in the rate of CO_2 evolution was seen as a result of this addition. The results from the soil respirometer studies strengthened the bacterial count findings, indicating that an active indigenous population of microorganisms is present at the Harbor Point site.

Screening Biological Activity in Batch Reactors. After reviewing the results from the preliminary chemical and microbiological analyses, it was decided to operate two "initial screening" batch reactors, one fed a mixture of leachate and soil (designated unit 1) and the other (unit 2) fed the low COD leachate. The two 3.85l

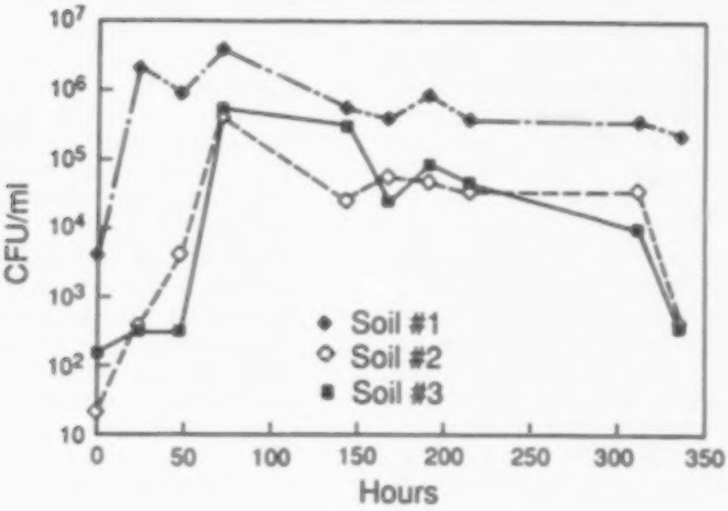


Figure 1. Semilog Plot of Growth of Indigenous Bacteria in Soil Samples.

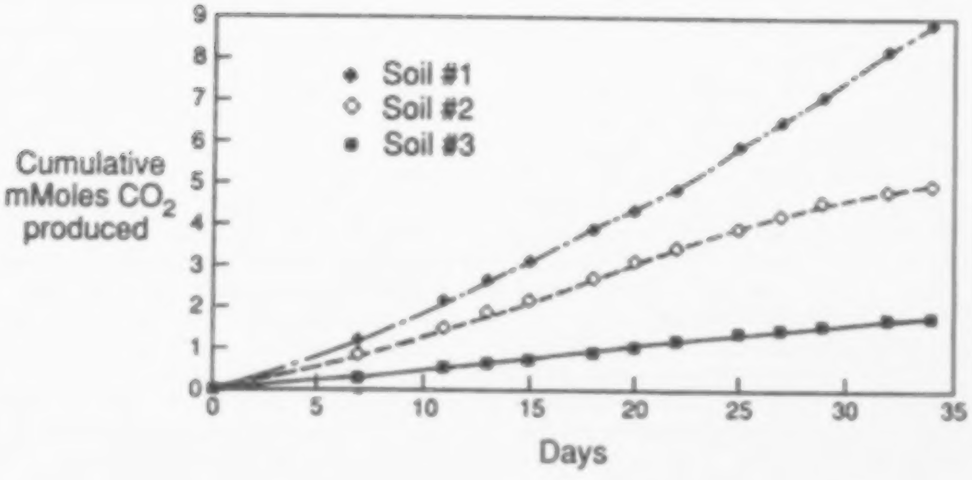


Figure 2. Cumulative CO_2 Evolution of Soils.

reactors were operated on an instantaneous fill and draw basis. Performance and biological activity was measured mainly by feed/effluent COD balances and by Oxygen Uptake Rate (OUR) measurements. The OUR test served as an excellent indicator for activity inhibition caused by sudden shock loading. Sporadic gas chromatograph analyses of selected target organics generally showed agreement with the overall COD removal trends.

Additional information regarding biological activity in the laboratory reactors was obtained from bacterial plate counts on the mixed liquor suspended solids (MLSS). The plating medium was TSA with various additional amounts of cyanide, one of the components of the contaminated soils. The results of these counts are summarized in Figure 3. As can be seen, a population of cyanide resistant bacteria that reached a stable population in number was selected in the reactors. The number of bacteria determined at each cyanide concentration was essentially the same for increasing cyanide levels. Indeed, bacterial counts in the 10^6/ml range were determined on the highest cyanide concentration, 100 mg/l KCN. Medium containing 1000 mg/l KCN was tried but no growth was detected at this level at any dilution of biomass.

Bench Scale SBR Operation. Based on the experience gained by the operation of the two batch reactors, four SBR units were established and operated simultaneously. Each reactor had a total liquid volume of 3.85l and received a biomass inoculum which was composed of a mixture of domestic sewage sludge and the remaining sludge from the two batch reactors. All four reactors were operated at room temperature (19 to 21C). The basic feed solution was prepared by mixing of 12l of tap water with 240g of contaminated soil for three days followed by 30 minutes of clarification. This feed solution contained low levels of soluble COD, ranging from 30 to 75 mg/l. However, the total COD readings were between 350 and 900 mg/l and the suspended solids concentrations ranged from 250 to 600 mg/l. Air to the reactors was introduced through porous diffuser stones. During anaerobic periods magnetic stirrers were used for mixing. All aeration, mixing, and discharge functions were sequenced with laboratory timers. Reactor operating conditions established after an initial acclimation period of three weeks are summarized in Table 1.

The basic feed of leachate plus soils was supplied to both the instantaneous fill units 1 and 2 and the continuous fill units 3 and 4 (supplied by piston pumps) during the initial acclimation period with a gradual increase to the levels described in Table 1. Nitrate nitrogen was added to units 1 and 2 which were kept anaerobic (i.e. mixing only was provided throughout the 22 hour react period) in order to develop a denitrifying bacteria population. During the acclimation period it was discovered that units 3 and 4 developed a nitrifying population which resulted in extreme pH decreases. As a result, the original operating mode of units 1 and 2 was altered to include the 5 hour aeration period shown in Table 1. This was done in order to promote nitrification followed by denitrification without external supplement of nitrate. In order to insure a sufficient supply of nitrogen and phosphorus and to conduct the appropriate denitrification oriented studies, these nurtients were daily added to the four reactors. Units 3 and 4 were supplied with additional alkalinity in order to promote nitrification and to minimize pH fluctuations. Table 1 summarizes the composition and amounts of the strengthening constituents added to the biological reactors. Glucose was chosen to be the additional carbon source for units 2 and 4 for its known tendency to form cyanohydrin with the cyanide ion. The cyanohydrins are reported to hydrolyze to aldonic acids which can serve as carbon and energy source for either aerobic or anoxic bacteria (17,19,20).

Operation of the SBR units was monitored by routine sampling and bi or tri weekly analyses of COD, MLSS, MLVSS, effluent suspended solids (total and volatile), ammonia, and nitrate and nitrite. The soluble effluent COD was in the range of 15 to 40 mg/l reflecting high removal of the waste organic constituents. Moderate sludge wastage resulted in increased levels of MLSS. This increase in suspended solids was due to bacterial growth and to the high influx of suspended materials in the feed. As expected, units 2 and 4 had a high yield of solids (because glucose is added to the feed) and units 1 and 3 had poor yield in spite of having high removal efficiencies for most constituents. This low yield for leachates containing toxic materials was observed by others (24) and may be explained by high maintenance energy requirements that results in catabolism of large amounts of substrate carbon to CO_2 and less assimilation into new cell mass. In general, the reactors' effluents were turbid with high levels of suspended solids that probably resulted from the oily nature of the feed mixture. Units 2 and 4, the glucose augmented systems, however, developed better clarification with lower levels of effluent suspended solids. Indeed, the glucose served as a means for improving settling characteristics of the sludge, perhaps by stimulating growth of flocculating bacteria or by contributing to higher production of extracellular polymers assisting in bioflocculation.

The variation of nitrogen compound concentrations in the reactors' effluents is shown in Figure 4. The influent ammonia nitrogen concentration for units 1 and 2 was 132 mg/l and was 100 mg/l for units 3 and 4. As can be seen from Figure 4, nitrification easily developed in all four reactors with highest levels found in units 3 and 4 which were supplied with additional alkalinity and the poorest performance being observed in unit 1, the reactor with neither glucose nor alkalinity being added to the feed. It appears that nitrifiers developed due to the protection of cyanide degraders in the mixed slurry, as also evidenced elsewhere (9). Denitrification was found to be inconsistent. This is not surprising since none of the reactors were operated in a manner that would optimize denitrification. In particular, alternating aerobic/anaerobic sequences during the fill period in SBR systems is necessary in order to achieve high nitrogen removal efficiency (18). While units 1 and 2 had the potential for developing denitrification, only unit 2 had sufficient carbon (i.e. glucose) added to drive the denitrification oriented reactions. It should be noted, however, that these units did develop denitrification capabilities during the initial acclimation period when nitrate was added to the feed and the reactors were maintained anaerobic.

GC analyses and cyanide determinations were conducted on the feed and effluent. Representative GC fingerprints for the phenols and the PNAs are given in Figure 5. As can be seen from this figure, these compound groups were easily removed in all four reactors even though the reactors were operated with markedly different strategies. A comparison of soluble and total effluents can be seen in Figure 5 for SBR unit 4. GC analyses for the purgeable aromatics both for the leachate feed and the effluent resulted in undetectable levels of these compounds. As a result, their removal, if any, could not be determined. Detailed data for some of the target organics and for cyanide, COD and ammonia are presented in Table 2. The quantitative analyses for the phenols and PNAs verify the qualitative trends shown in Figure 5, and also agreed with the COD removal efficiencies. Cyanide removal efficiencies were generally satisfactory. However, the differences between the four SBR units could not be attributed to the different operating conditions.

SUMMARY

While the leachates and soils from Harbor Point are contaminated with organics that are known to be toxic to some microorganisms, indigenous bacteria which can tolerate and degrade these constituents were found to be present and survive even without the development of optimal conditions for nutrients, aeration and organism density. Bacterial strains were developed in SBR units which were shown to be flexible in operation and easily maintained on the constituents of the leachates and soils from Harbor Point and are therefore likely to be an excellent source of "Specialized Bacteria" inoculum

Table 1 - Summary of Operating Conditions Following Initial Three Week Acclimation Period.

	Unit1	Unit2	Unit3	Unit4
Max. Reactor Liquid Vol., L	3.85	3.85	3.85	3.85
Daily Feed Volume , L	0.5	0.5	1.0	1.0
Detention Time , Days	7.7	7.7	3.85	3.85
Supplemental Components Added to Basic Feed*, mg , for:				
Glucose as COD	0	600	0	600
Ammonia Nitrogen as N	64	64	96	96
Phosphorous as P	10	10	15	15
Alkalinity as $CaCO_3$	0	0	600	600
Time in Hours, for:				
Aerated Fill	0	0	6	6
Mixed Fill	0.01	0.01	0	0
Mixed React	17	17	0	0
Aerated React	5	5	16	16
Settle	1.5	1.5	1.5	1.5
Draw & Idle	0.5	0.5	0.5	0.5
Cycles per Day	1	1	1	1

*Basic Feed was composed of leachate and contaminated soils obtained after mixing 12L of tap water with 240g of soil for 3 days followed by 30 minutes of clarification. Feed concentration of total COD ranged from 350 to 900 mg/l and that of suspended solids, from 250 to 600 mg/l.

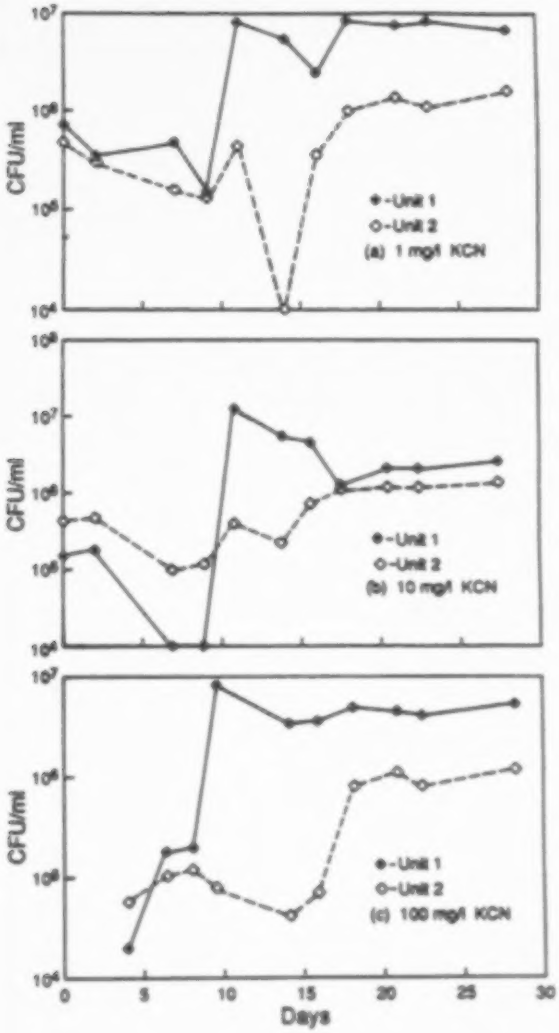


Figure 3. Bacterial Counts on MLSS from the "Initial Screening" Reactors on TSA + KCN.

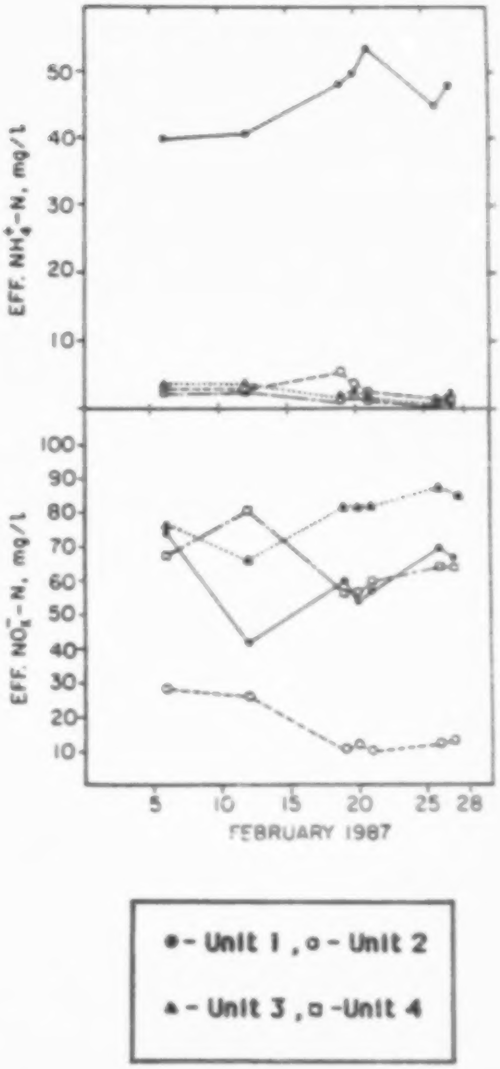


Figure 4. Chronological Plot of SBRs Effluent Ammonia and Oxidized Nitrogen.

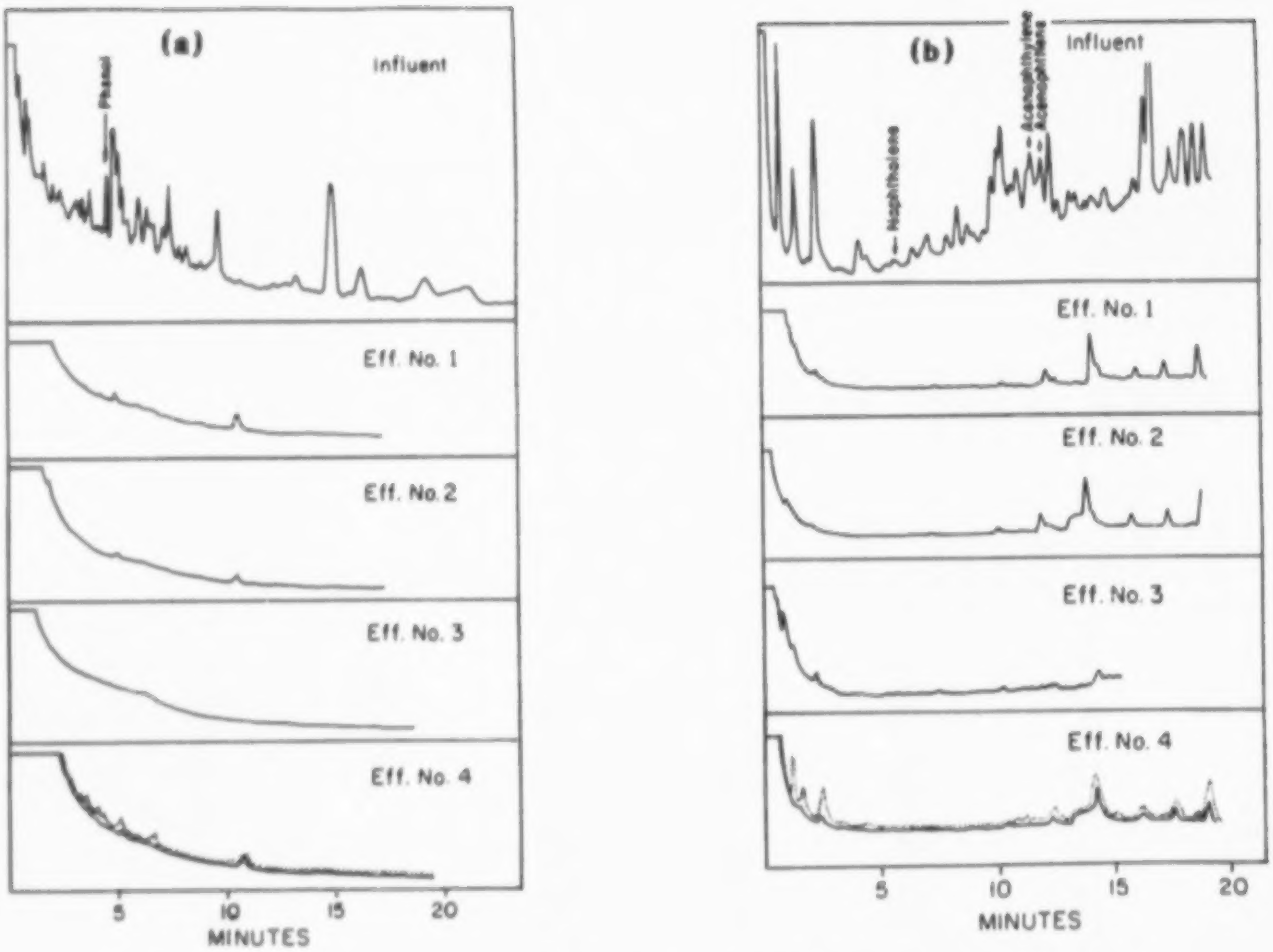


Figure 5. GC-FID Fingerprints of the Phenols (a) and the Polynuclear Aromatic Hydrocarbons (b). (Influent is Total. Dotted Line for Eff. No. 4 is Total. All Other Effluents (Solid Lines) are for Soluble. Sampling Date: 1/14/87).

Table 2 - Removal of Specific Constituents in the SBR Units(Average Values for January 14-16,87).

Contaminant		(1) Influent	(2) Effluent
COD , mg/l			
	Unit#1	500	35.0
	Unit#2	1700	34.0
	Unit#3	500	30.0
	Unit#4	1100	32.0
Ammonia,mg/l as N			
	Unit#1	132.2	11.9
	Unit#2	132.2	2.5
	Unit#3	100.2	1.7
	Unit#4	100.2	1.8
Cyanide,mg/l as CN			
	Unit#1	28.6	2.9
	Unit#2	28.6	3.8
	Unit#3	28.6	7.0
	Unit#4	28.6	2.6
Phenol , ug/l			
	Unit#1	13.1	0.5
	Unit#2	13.1	<0.14
	Unit#3	13.1	<0.14
	Unit#4	13.1	<0.14
Acenaphthene,ug/l			
	Unit#1	47.8	1.9
	Unit#2	47.8	2.3
	Unit#3	47.8	<1.8
	Unit#4	47.8	<1.8
Acenaphthylene,ug/l			
	Unit#1	99.5	<2.3
	Unit#2	99.5	<2.3
	Unit#3	99.5	<2.3
	Unit#4	99.5	<2.3
Naphthalene,ug/l			
	Unit#1	17.5	<1.8
	Unit#2	17.5	<1.8
	Unit#3	17.5	<1.8
	Unit#4	17.5	<1.8

(1) - Total , Except for Ammonia.
(2) - Soluble , Except for Cyanide.

for in-situ soil remediation programs.

REFERENCES

1. APHA, AWWA, WPCF, 1985, Standard Methods for the Examination of Water and Wastewater, 16th Ed.

2. Bryan, E.H., 1982, "Research on Innovative Concepts in Treatment of Wastewater and Management of Residual Sludges," presented at the North Carolina American Water Works Association - Water Pollution Control Association, Annual Meeting, Greensboro, NC.

3. Cerniglia, C.E., 1984, "Microbial Metabolism of Polycyclic Aromatic Hydrocarbons," Advances in Applied Microbiology, 30, 31.

4. Chiesa, S.C., Irvine, R.L., 1985, "Growth and Control of Filamentous Microbes in Activated Sludge: An Integrated Hypothesis," Water Research, 19, 471.

5. Chiesa, S.C., Irvine, R.L., and Manning, Jr., J.F., 1985, "Feast/Famine Growth Environments and Activated Sludge Population Selection," Biotechnology and Bioengineering, 27, 562.

6. EPA, 1984, Federal Register, 40 CFR Part 136, Vol. 49, No. 209.

7. EPA Technology Transfer, 1982, The Bridge Between Research and Use, EPA-600/D-82-331.

8. Hach Company, 1984, Procedures for Water and Wastewater Analysis, 2nd Ed.

9. Harden, D., Jones, D.D. and Gauthier, J.J., 1983, "Adaptation of an Industrial Activated Sludge Process to the Removal of Cyanide," Proc. 38th Purdue Industrial Waste Conference, Ann Arbor Science.

10. Herzbrun, P.A., Irvine, R.L., Malinowski, K.C. and Hanchak, M.J., in press, "Treatment of Hazardous Wastes in a Sequencing Batch Reactor," Biotechnology Applied to Environmental Problems, ed. by D.L. Wise, CRC Press, Inc.

11. Herzbrun, P.A., Irvine, R.L. and Malinowski, K.C., 1985, "Biological Treatment of Hazardous Waste in the SBR," Journal Water Pollution Control Federation, 57, 1163.

12. Irvine, R.L., Ketchum, Jr., L.H., Breyfogle, R. and Barth, E.F., 1983, "Municipal Application of Sequencing Batch Treatment at Culver, Indiana," Journal Water Pollution Control Federation, 55, 484.

13. Irvine, R.L., Sojka, S.A. and Colaruotolo, J.F., 1984, "Enhanced Biological Treatment of Leachates from Industrial Landfills," Hazardous Wastes, 1, 123.

14. Irvine, R.L., 1985, "Project Summary. Technology Assessment of Sequencing Batch Reactors," EPA/600/S2-85/007.

15. Irvine, R.L., Ketchum, Jr., L.H., Arora, M.L. and Barth, E.F., 1985, "An Organic Loading Study of Full-Scale Sequencing Batch Reactors," Journal Water Pollution Control Federation, 57, 847.

16. Knowles, C.J. and Bunch, A.W., 1986, "Microbial Cyanide Metabolism," Advances in Microbial Physiology, 27, 73.

17. Lewandowski, Z., 1984, "Biological Denitrification in the Presence of Cyanide," Water Research, 18, 289.

18. Palis, J.C. and Irvine, R.L., 1985, "Nitrogen Removal in a Low-Loaded Single Tank Sequencing Batch Reactor," Journal Water Pollution Control Federation, 57, 82.

19. Raef, S.F., Characklis, W.G., Kessick, M.A. and Ward, C.H., 1977a, "Fate of Cyanide and Related Compounds in Aerobic Microbial Systems - I. Chemical Reaction with Substrate and Physical Removal," Water Research, 11, 477.

20. Raef, S.F., Characklis, W.G., Kessick, M.A. and Ward, C.H., 1977b,

"Fate of Cyanide and Related Compounds in Aerobic Microbial Systems - II. Microbial Degradation," Water Research, 11, 485.

21. Stamoudis, V.C. and Luthy, R.G., 1980, "Determination of Biological Removal of Organic Constituents in Quench Waters from High-BTU Coal-Gasification Pilot Plants," Water Research, 14, 1143.

22. "Superfund Strategy", 1985, Washington, DC: Congress, Office of Technology Assessment, OTA-ITE-252, pg. 211.

23. U.S. Environmental Protection Agency, 1983, Process Design Manual for Land Application of Municipal Sludge, EPA-625/1-83-016.

24. Venkataramani, E.S. and Ahlert, R.C., 1984, "Rapid Aerobic Biostabilization of High-Strength Industrial Landfill Leachate," Journal Water Pollution Control Federation, 56, 1178.

25. Visilind, P.A., Hartman, G.C. and Skene, E.T., 1985, Sludge Management and Disposal, Lewis Publishers, Inc., Chelsea, Michigan.

Disclaimer

The work in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

WHITE ROT FUNGUS DETOXIFICATION RESEARCH
STATUS AND DIRECTIONS

John A. Glaser and Pasquale R. Sferra

United States Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

ABSTRACT

Some of the more common substructures of lignin, catechol diethers, alkylarenes, and biphenyls, resemble the chemical structure of many persistent organic compounds contaminating the environment. The remarkable similarity in structure led several investigators to research the applicability of a white rot fungus, Phanerochaete chrysosporium, to the biodegradation of hazardous waste constituents.

Starting in 1984, the Hazardous Waste Engineering Research Laboratory of the U.S. Environmental Protection Agency has funded research to determine the feasibility of using P. chrysosporium to degrade organic pollutants.

The white rot fungus research continues to stimulate interest and shows promise for field applications. The parts of the research program sponsored by the Hazardous Waste Engineering Research Laboratory are starting to develop major advances in the emerging biological control technology field.

INTRODUCTION

White rot fungi are primary wood degraders in nature (1). All components of wood are degraded by these fungi including lignin which is a structural component of wood composed of a heteropolymer formed from the cross linking of three precursor cinnamyl alcohols (2).

The structural features of lignin dictate unusual constraints on the biodegradation systems responsible for the initial attack on lignin. The 600-1000 k-dalton size range for lignin is far too large to enter cells. The requirements are that the degradative system must be extracellular, non-specific, and non-hydrolytic. Analogies with other biopolymers degrading systems fail since these other systems are hydrolytic and specific (2).

Some of the more common substructures of lignin, catechol diethers, alkylarenes, and biphenyls, resemble the chemical structure of many persistent organic compounds contaminating the environment. The remarkable similarity in structure led several investigators to research the applicability of a white rot fungus, *Phanerochaete chrysosporium*, to the biodegradation of hazardous waste constituents (2).

Since the findings of Aust (3) and Eaton (4), the area of application of the white rot fungus, *P. chrysosporium*, to the detoxification of organic compounds designated as hazardous waste constituents has progressed significantly. Starting in 1984, the Hazardous Waste Engineering Research Laboratory of the U.S. Environmental Protection Agency has funded research to determine the feasibility of using *P. chrysosporium* to degrade organic pollutants.

Data on degradation by white rot fungus have resulted from the Michigan State University research team's efforts (now at Utah State University) and more recently the new experimental approaches of the USDA Forest Products Laboratory and the State University of New York at Syracuse. This research sponsored by the USEPA represents a structured, target directed program of individual projects focusing on the short term application of this microorganism to a field setting for treatment of contaminated soil and water.

COMPETENCE AND NUTRITIONAL STUDIES (5)

In the first report of this work, Bumpus *et al.* (3) showed that the fungus oxidized 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT), 3,4,3',4'-tetrachlorobiphenyl, 2,4,5,2',4',5'-hexachlorobiphenyl, 2,3,7,8-tetrachlorodibenzo[p]dioxin (TCDD), lindane, and benzo(a)pyrene to carbon dioxide. Subsequent investigations showed that the fungus is capable of mineralizing hexachlorobenzene, Mirex, Aroclor 1242 (6), Aroclor 1254 (4, 7), chlordane, pentachlorophenol, p-cresol, phenanthrene, 2-methylnaphthalene, and biphenyl (7), benzoic acid (8), and Atrazine, naphthalene, and methoxychlor (9).

DDT was used as a model compound for detailed biodegradation experiments (10). In this work determinations were made on DDT disappearance, metabolite identification, mass balance analysis, and ^{14}C-DDT mineralization and it was found that *P. chrysosporium* causes extensive degradation of DDT in nutrient nitrogen-deficient cultures. The metabolites from DDT that were identified included 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (dicofol), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD), 2,2-dichloro-1,1-bis(4-chlorophenyl)ethanol (FW-152), and 4,4'-dichlorobenzophenone (DBP). These results allowed for the determination of a proposed pathway different from the major pathway proposed for bacterial degradation of DDT occurring in the environment. In this work it was determined that other fungi, *Pleurotus ostreatus*, *Phellinus weirii*, and *Polyporus versicolor*, also mineralized DDT.

It was found that with glucose as a growth substrate the rate and extent of DDT mineralization increased with increasing glucose concentration (11, 12). This held true for the glucose test concentrations between 23 mM and 112 mM. The greatest initial rate of mineralization, however, occurred when the organism was grown on 23 mM glucose. Also, as the concentration of glucose became limiting the rate of mineralization quickly declined.

Alternative growth substrates differed in their effects upon DDT mineralization (9). Glucose, fructose, mannose, mannitol, and glycerol supported growth and mineralized DDT while polyethylene glycol, glycine, and benzoic acid did not support growth of the fungus or mineralization of DDT. Cellulose, a growth substrate for the fungus in nature, under experimental conditions increased the amount of DDT mineralization approximately two fold relative to glucose. The authors suggested that more efficient growth and mineralization of organic pollutants may be possible when the fungus is grown on cellulose because of the organism's ability to regulate the availability and utilization of glucose.

Hydrogen peroxide, a required cofactor/activator of ligninases, can be produced by a number of carbohydrate oxidases and other enzymes in wood rotting fungi. It is known that a major source of hydrogen peroxide is the glucose oxidase system when glucose is the growth substrate (9). It is believed then that mineralization of organic pollutants is dependent upon the ability of the fungus to generate H_2O_2. Ongoing research is attempting to determine the specifics of the action of H_2O_2 on growth and degradation.

ENZYME STUDIES

Among the more important reactions in lignin breakdown by P. chrysosporium are cleavage of the lignin alkyl side chain, ring demethylation, and ring cleavage. The alkyl side chain cleavage is catalyzed by a hemoprotein ligninase that was discovered in 1983. Hydrogen peroxide is consumed in this reaction with corresponding changes in the enzyme absorption spectrum during catalysis attributable to resting states-compound I-compound II spectral transients indicating a peroxidative mechanism (12). Stoichiometries of product formation as well as hydrogen peroxide and oxygen uptake are consistent with a radical pathway (13). These results established the one-electron oxidative mechanism as the primary extracellular oxidative pathway for P. chrysosporium.

It has been shown that P. chrysosporium produces at least ten extracellular hemoproteins and roughly half have ligninase activity (14). The enzyme component designated H8 has been used by several researchers to characterize the ligninase activity. Depending on growing conditions, H8 can be displaced as the major component in favor of H2. The extracellular hemoproteins have distinct amino acid sequences hence they are separate gene products and not merely degradation products of a single precursor.

The heme componments H3-H5 have manganese peroxidase activity. This three component fraction catalyzes a hydrogen peroxide-dependent oxidation of Mn(II) to Mn(III) but lacks the specificity of H8 to cleave the alkyl side chains. Two reports (15, 16) of soluble manganese ion acceleration on this fraction prompted further inspection of the enzymatic activity of these peroxidases. The current status of this research is unclear with respect to the reported accelerations. Spectral contamination has been observed that contributes to a complex situation for rate data interpretation.

The heterogeneity among the various extracellular proteins produced by P. chrysosporium points to possible functional differences among them important to pollutant degradation. There presently are attempts to uncover substrate specificities where information indicates that they may exist.

The ability of the ligninase H8 to oxidize polynuclear hydrocarbons has been related to the ionization potential of these compounds. When pyrene is used as a substrate with H8 both pyrene-1,6-dione and pyrene-1,8-dione are the major products. In similar fashion, anthracene is converted to anthraquinone and benz(a)anthracene yields 7,12-benz(a)anthraquinone (17). Both the pyrene-1,6-dione and pyrene-1,8-dione are mutagenic by the Ames test. When the compounds are presented as substrates to the fungus these diones do not accumulate.

Dibenzodioxin and 2-chlorodibenzodioxin are oxidized by the H8 ligninase in the presence of hydrogen peroxide (17). Only determination of radical cation intermediates by flow cell ESR studies was made for these compounds without any product identification. Current work is directed to determine whether chlorinated aromatics are substrates (18, 19). Chlorinated phenols have been found to be very suitable substrates, and product identification is under way (20).

SOIL STUDIES (21, 22)

The general success of solution biodegradation studies with the fungus stimulated speculation that this microorganism may be an appropriate candidate for the treatment of contaminated soils. A research program was initiated with the USDA Forest Products Laboratory designed to specifically investigate and develop a soil treatment system based on the white rot fungus. Research to date has assessed the effects of selected soil types, temperatures, pH, and water potentials on the growth of the fungus in sterile and non-sterile soils. Biomass accumulations as well as growth habits of P. chrysosporium were greatly influenced by soil type. Soil nitrogen content appears to be the primary factor responsible for differences in fungal growth in three studied soils. Growth was strongly and positively correlated with nitrogen content. This factor, therefore, appears to play a major role in mediating the growth of the fungus in the soil, and is easily controlled by nitrogen supplementation.

Increasing the soil water potential from -1.5 MPa to -0.03 MPa resulted in greatly increased growth of P. chrysosporium. Research data suggest that fungal growth might benefit from soil water potentials greater than -0.03 MPa. Water potential is another easily controlled soil factor.

Early work in this investigation indicated that P. chrysosporium did not grow well in non-sterile soils attributable in part due to ineffective competition with the indigenous microflora. Lately it has been found that growth within the soil can be accomplished through the use of larger quantities of inoculum. These results were anticipated since the soil is not the normal habitat of P. chrysosporium.

The white rot fungus grows over a wide range of temperatures. Growth has been assessed from 10-39°C. No growth was observed at 10°C whereas growth significantly increases with temperature from 15 to 30°C. No significant difference in growth was recorded from 30 to 39°C. Soil temperatures under field conditions can be controlled by selecting the normal warm months and by soil solarization.

Future investigations in the soil application research will include small scale treatment of selected pollutants at environmentally significant concentrations, the evaluation of growth stimulating amendments on primary and secondary metabolism, and the delivery of oxygen to the growing fungus within the soil column. Ancillary investigations will include the development of analytical procedures to assay the fungal growth within the soil, the importance of soil sterilization to growth of the fungus, and inoculum development.

TECHNOLOGY DEVELOPMENT

A water treatment process developed jointly by North Carolina State University and the USDA Forest Products Laboratory will be investigated in the next year at the bench and scaled up to determine its treatment efficacy. The patented reactor (23) is a specially designed rotating biological contactor that utilizes P. chrysosporium as the biological species for treatment. Recent results derived for the operation of this technology show that this reactor will degrade 250 ppm pentachlorophenol in water to 5 ppm in 8 hours (24). Pink water associated with munitions production is adequately treated. Degradation of 2,4,6-trinitrotoluene and 2,4-dinitrotoluene is observed in concentrations up to 150 ppm in 24 hours (24).

CONCLUSIONS

White rot fungus research continues to stimulate interest and shows promise for field applications. The parts of the research program sponsored by the Hazardous Waste Engineering Research Laboratory are starting to develop major advances in the emerging biological control technology field.

Additional research will be pursued to increase the potential for white rot fungus as a practical degrader of hazardous pollutants. Possible programs for consideration as future research areas are the selection for strains that are high producers of ligninases, selection for strains capable of producing ligninases regardless of the nutrient starvation requirement, and optimizing culture conditions for ligninase production. Enzyme production is expected to be improved by means of gene cloning techniques. The cDNA for a ligninase from P. chrysosporium has already been cloned and sequenced (25). This accomplishment shortens the time it will take to develop, by means of biotechnology techniques, super producers of the white rot fungus enzymes that are so effective as pollutant degraders.

REFERENCES

1. Kirk, T.K. and M. Shimada.1985. pp 579-605. In Biosynthesis and Biodegradation of Wood Components, T. Higuchi Ed. Academic Press, N.Y.

2. Kirk, T.K. 1984. Degradation of Lignin. pp 399-438. In Microbial Degradation of Organic Compounds, D.T. Gibson, Ed., Marcel Dekker.

3. Bumpus, J.A., M. Tien, D. Wright, and S.D. Aust. 1985. Oxidation of Persistent Environmental Pollutants by a White Rot Fungus. Science, 228, 1434-1436.

4. Eaton, D.C. 1985. Mineralization of polychlorinated biphenyls by Phanerochaete chrysosporium: a ligninolytic fungus. Enzyme Microb. Technol., 7:194-196.

5. Bumpus, J.A., and S.D. Aust. 1987. Biodegradation of Environmental Pollutants by the White Rot Fungus Phanerochaete chrysosporium: Involvement of the Lignin Degrading System. BioEssays, 6:166-170.

6. Bumpus, J.A., and S.D. Aust. 1987. Biodegradation of Chlorinated Organic Compounds by Phanerochaete chrysosporium, A Wood Rotting Fungus. In: Solving Hazardous Waste Problems, J.H. Exner, Ed., American Chemical Society Symposium Series 338, pp. 340-349.

7. Bumpus, J.A., and S.D. Aust. 1987. Mineralization of Recalcitrant Environmental Pollutants by a White Rot Fungus. In: *Proceedings of the National Conference on Hazardous Wastes and Hazardous Materials*, March, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 146-151.

8. Bumpus, J.A., and S.D. Aust. 1987. Biological Oxidations by Enzymes from a White Rot Fungus, AIChE Symposium Publication (In press).

9. Aust, S.D., and J.A. Bumpus. 1987. Biodegradation of Halogenated Hydrocarbons. *Environmental Research Brief*, EPA/600/M-87/012.

10. Bumpus, J.A., and S.D. Aust. 1987. Biodegradation of DDT [1,1,1-Trichloro-2,2-Bis(4-Chlorophenyl)Ethane] by the White Rot Fungus *Phanerochaete chrysosporium*. *Applied and Environmental Microbiology* (In press).

11. Bumpus, J.A., M. Tien, D. Wright, and S.D. Aust. 1985. Biodegradation of Environmental Pollutants by the White Rot Fungus *Phanerochaete chrysosporium*. pp. 120-126. *Symposium Proceedings*, USEPA Eleventh Annual Research Symposium on Toxic Waste Disposal, April, Cincinnati, OH, EPA/600/9-85/028.

12. Bumpus, J.A., and S.D. Aust. 1985. Studies on the Biodegradation of Organopollutants by a White Rot Fungus. pp. 404-410. *Proceedings International Conference on New Frontiers for Hazardous Waste Management*, September, Pittsburgh, PA, EPA/600/9-85/025..

13. Hammel, K.E., M. Tien, B. Kalyanaraman, and T.K. Kirk. 1985. Mechanism of oxidative C-C cleavage of a lignin model dimer by *Phanerochaete chrysosporium* ligninase: Stoichiometry and involvement of free radicals. *J. Biol. Chem.* 260:8348-53.

14. Kirk, T.K., S. Croan, M. Tien, K.E. Murtaugh, and R.L.Farrell. 1986. Production of multiple ligninases by *Phanerochaete chrysosporium*: Effect of selected growth conditions and use of mutant strain. *Enz. Microb. Tech.* 8:27-32.

15. Glenn, J.K., and M.H. Gold. 1985. Purification and Characterization of an Extracellular Mn(II)-Dependent Peroxidase from the Lignin-Degrading Basidomycete, *Phanerochaete chrysosporium*, *Arch. Biochem. Biophys.* 242:329-341.

16. Paszczynski, A., V.-B. Huynh, and R. Crawford. 1986. Comparison of Ligninase-I and Peroxidase-M2 from the White Rot Fungus *Phanerochaete chrysosporium*. *Arch. Biochem. Biophys.* 244:750-765.

17. Hammel, K.E., B. Kalyanaraman, and T.K. Kirk. 1986. Oxidation of polycyclic aromatic hydrocarbons and dibenzo[p]dioxins by *Phanerochaete chrysosporium* ligninase. *J. Biol. Chem.* 261:16948-52.

18. Hammel. K.E., T.K. Kirk, B. Kalyanaraman, and J.A. Glaser. 1987. Oxidation of Persistent Aromatic Pollutants by Lignin Degrading Enzymes. (To be published in the Proceedings of the 13th Annual Hazardous Waste Symposium, Cincinnati, OH).

19. Hammel, K.E., B. Kalyanaraman, and T.K. Kirk. 1987. Oxidation of Aromatic Pollutants by Phanerochaete chrysosporium Ligninase. Proceedings 194th National American Chemical Society Meeting, New Orleans, LA.

20. Hammel, K.E., B. Kalyanaraman, and T.K. Kirk. 1987. Oxidation of Aromatic Pollutants by Phanerochaete chrysosporium ligninase, Proceedings of International Seminar on Lignin Enzymic and Microbial Degradation, Paris.

21. Lamar, R.T., M.J. Larsen, T.K. Kirk, and J.A. Glaser. 1987. Growth of the white-rot fungus Phanerochaete chrysosporium in soil. (to be published in the Proceedings of the 13th Annual Hazardous Waste Symposium, Cincinnati, OH).

22. Lamar, R.T., M.J. Larsen, T.K. Kirk, and J.A. Glaser. 1987. Effect of Biotic and Abiotic Soil Factors on Growth and Degradative Activity of the White Rot Fungus Phanerochaete chrysosporium Burds. Proceedings of the 194th National American Chemical Society Meeting, New Orleans, LA.

23. Chang, H.-M., T.W. Joyce, T.K. Kirk, and V.-B. Huynh. 1985. U.S. Patent No. 4,554,075.

24. Joyce, T.W., H.-M.Chang, B. Vasudevan, and H. Taneda. 1987. Degradation of Hazardous Organics by the White Rot Fungus Phanerochaete chrysosporium. Proceedings of the 194th National American Chemical Society Meeting, New Orleans, LA.

25. Tien, M., and C.-P. D. Tu. 1987. Cloning and sequencing of a cDNA for a ligninase from Phanerochaete chrysosporium. Nature 326:520-523.

OCEAN DISPOSAL OF SOLIDIFIED/STABILIZED HAZARDOUS WASTES

Paul L. Bishop and Kristine L. Melchinger
Department of Civil Engineering
University of New Hampshire
Durham, New Hampshire 03824

ABSTRACT

This research project investigated the feasibility of using the oceans as a repository for solidified/stabilized hazardous wastes. It was postulated that the oceans would be superior to land for disposal of these wastes because of the highly alkaline environment present in the oceans which would minimize heavy metal leaching. It was found that solidified/stabilized wastes placed into synthetic seawater leached at a much lower rate than wastes placed in a simulated groundwater. In fact, seawater leachate metal concentrations were almost always below the detection limit, even when the metals were first extracted with a chelating resin and then analyzed by graphite furnace atomic absorption spectrophotometry. It was also found that calcium and magnesium deposited in the pores and on the surfaces of the waste forms, thereby reducing leaching rates even further. The results suggest that marine disposal of solidified/stabilized wastes may be a feasible solution to many of our hazardous waste disposal problems.

INTRODUCTION

Despite current bans on marine disposal of most hazardous wastes, interest in use of the oceans as a repository for these wastes is growing. The no-ocean-dumping policy now in effect will certainly improve the quality of our ocean waters, but it is doing this at the expense of our very precious and limited ground and surface waters. Judicious use of the oceans could greatly minimize potentially irrevocable damage to our groundwaters by removing these wastes from possible contact with them. For the oceans to be acceptable as a site for waste disposal, though, it must be proven that no detrimental impacts will result.

One way of minimizing potential damage from inorganic wastes is to solidify/stabilize the wastes with cement, fly ash and other additives so as to render them less likely to leach harmful contaminants. This is a relatively new process which converts a liquid, solid or semi-solid material into a solid monolith which is dimensionally stable and in which the contaminants are bound tightly so that their leaching rates are greatly reduced (1). The process has been used for disposal on land but has not been attempted in marine waters for wastes classified as hazardous. Marine disposal of these wastes has several potential advantages, though. Most metals which leach from solidified/stabilized wastes do so because of attack by aggressive groundwaters. However, seawater is alkaline, with a pH of about 8.3. In addition, there is evidence that magnesium in seawater will deposit as insoluble precipitates in the pores of the solidified wastes, reducing the waste's porosity over time (2,3). Finally, any metals which do leach will probably be rapidly diluted and dispersed into the oceans, thus minimizing any potential damage.

Little is known about the mechanisms causing metal binding in the cement matrix, but it is believed to be due to a combination of entrapment of insoluble metal precipitates in pores in the cement and within the cement matrix, and to adsorption to cement paste surfaces (5). Many heavy metals are bound into the pastes as metal hydroxides and metal silicates, and their solubility and resulting leachability are thus governed by the pore water pH. The solidified/ stabilized wastes have a large amount of free alkalinity and can buffer against pH change by acidic leachants, but eventually the acidity of acidic groundwaters can overcome this buffering capacity and metal leaching will occur.

PURPOSE

The purpose of this research was to begin an evaluation of the feasibility of ocean disposal of solidified/stabilized inorganic hazardous wastes. The intent was to examine rates of metal leaching from stabilized/ solidified wastes placed in a marine environment and compare these with corresponding rates from wastes placed in a simulated ground water environment. This research was conducted in a laboratory setting; current research is investigating in-situ disposal of these wastes in the ocean.

For this research, information was obtained concerning: 1) the effects of the heavy metals used on the physical and microstructural properties of the resulting waste form; 2) the effects of the leaching medium on properties of the waste form; and 3) the rates of leaching of metals and other chemical constituents from these waste forms when exposed to acidic groundwater and seawater. These data were then used to evaluate the potential environmental hazard due to contaminants leaching from these wastes in the ocean.

APPROACH

Synthetic metal hydroxide sludges were made containing cadmium, chromium, lead and combinations of these. The appropriate amounts of cadmium nitrate, chromium chloride and lead nitrate were dissolved in deionized water, and then a sludge was formed by addition of sodium hydroxide (6.0 M NaOH) to bring the solution pH to 8.5-9.0. This caused the metals to precipitate as their metal hydroxides. The metal concentrations in the individual metal sludges after pH adjustment were: 1) cadmium - 23,000 ppm (0.20 M), 2) chromium - 24,000 ppm (0.46 M), and lead - 23,000 ppm (0.11 M). A mixed metal sludge was also prepared containing 0.04 M of each metal (4500 ppm cadmium, 2080 ppm chromium, 8290 ppm lead).

Fixed waste samples were prepared by mixing the sludges with type II portland cement to form cement pastes with water/cement ratios (w/c) of 0.5 and 1.0. No water was added, as the water in the sludge was sufficient. The freshly mixed pastes were then poured into 4.0 cm diameter by 7.6 cm high PVC cylinders; these were sealed on the ends with glass plates. The cylinders were allowed to set for 24 to 48 hours at 100% humidity before they were removed from the molds and returned to the 100% humidity room. Further curing occurred for a minimum of 28 days. The samples were then ground with a mortar and pestle to a size of 5 to 10 mm.

The ground waste was leach tested using a modification of the procedure developed by Bishop (4) for solidified/stabilized wastes. 10 grams dry weight of the particles were added to 500 ml leachant in glass beakers covered with parafilm. The beakers were placed on a shaker table and mixed at a frequency of 120 cycles per minute with a 3.8 cm stroke. A synthetic sea water leachant was used which duplicated natural seawater very closely (34,000 ppm salinity, 18,788 ppm chlorinity). Additional leaching studies were performed using a weakly acidified leachant to simulate an acidic groundwater for comparison purposes (0.04 M acetic acid, pH = 5.0). Leaching continued for 50 days with the seawater leachant, with leachant being changed every 3 days. The acidified leachant samples were changed daily over a 15 day period. All leachates were analyzed for pH, alkalinity, cadmium, chromium and lead. A Perkin-Elmer model 2380 atomic absorption spectrophotometer with graphite furnace was used for metals analysis; the method of standard additions was employed. Because of interferences from the dissolved solids in the seawater leachates, it was necessary to first extract the metals from the leachate using Chelex 100 chelating resin. The procedure used is described by Bishop and Gress (2).

The effect of incorporation of heavy metals into cement paste and the effects of leaching by pure water and seawater on the microstructure of the cement paste was investigated by scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDAX). Representative particles were removed from deionized water and seawater leachants every 3 days over a 50 day leaching period. Fractured specimens of the paste were mounted on carbon stubs with carbon cement, dessicated and coated with carbon for EDAX analysis; later, they were coated with a thin layer of gold-palladium alloy for SEM micrographs.

PROBLEMS ENCOUNTERED

There were two major problems encountered in this research. The first was that there was no acceptable leaching test procedure available for this type of waste. Consequently, a leaching procedure had to first be developed. This is described elsewhere by Bishop (4,6). Secondly, the metal concentrations present in the seawater leachates were so small and the dissolved solids interferences were so high that it became necessary to go to a very laborious ion exchange extraction procedure for the heavy metals before analysis. This procedure is described by Bishop and Gress (2).

RESULTS

Stabilized/solidified wastes were first leach tested with a mildly acidified leachant to simulate groundwater leaching. These results have been reported previously (2,4,5,7,8) and will only be summarized here. Based on numerous experiments employing sequential batch extractions for a 15 day period, it was found that the waste contained a large amount of free alkalinity which buffered against pH changes. Even though the leachant pH was 5.0, the leachate pH remained very high until after large amounts of acid had been added and this alkalinity had been neutralized (Figure 1). Consequently, leaching took place under an alkaline rather than an acidic environment for many days of leaching. The result was that heavy metal leaching was minimal until the pH of the leachate dropped below about 6.0 (Figure 2). After this, metal leaching rates increased rapidly, with the rate of leaching dependent upon the metal evaluated. Cadmium leached much more rapidly than lead; chromium leached very little, even after extensive leaching. Additional studies indicated that the metals were bound into the paste as hydroxides and silicates, with the majority of the chromium and lead present as silicates. Consequently, metal leaching did not become appreciable

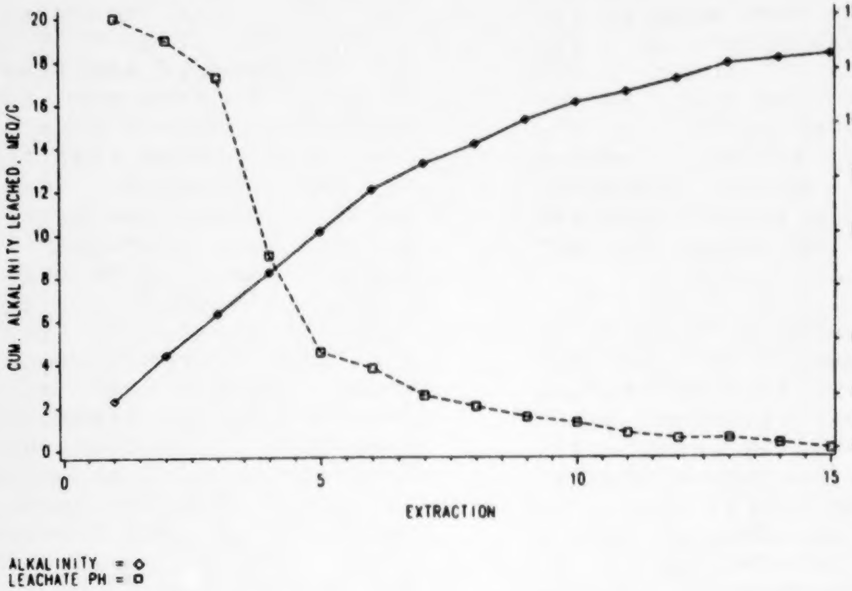


Figure 1. Leachate pH and cumulative alkalinity from solidified/stabilized wastes leached with an acidified leachant.

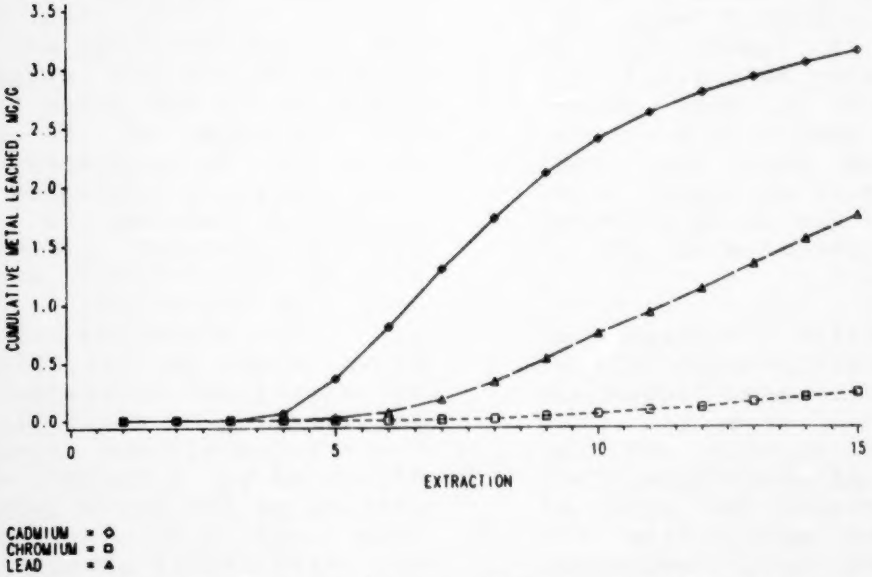


Figure 2. Cumulative cadmium, chromium and lead masses leached from solidified/stabilized wastes with an acidified leachant.

until the pH became low enough to dissolve these precipitates. After 15 sequential extractions, much of the metals originally in the waste were still there - 85% of the chromium and 75% of the lead were still in the silica rich solids. Cadmium was much more soluble, though, and only 8% remained in the solids after 15 extractions.

The tendency for a given metal to leach from a particular stabilized/solidified waste can be estimated using the "Leachability Index" (LX) which describes the diffusivity of the metal in the waste. The LX concept and a method for determining it in solidified/stabilized wastes can be found elsewhere (4,6). The LX index is a dimensionless term which can be used to compare the relative mobility of different contaminants on a uniform scale that varies from 5 (very mobile) to 15 (immobile). LX values were determined for wastes used in this study. Using the acetic acid leachant, it was found that cadmium had a LX of about 10.9, while lead had an LX of about 11.2 and chromium an LX of 14.0.

Extensive testing of these stabilized/solidified wastes was then performed in seawater to ascertain the effect of seawater on the chemistry of the waste form and to measure the rate of leaching of metals from the waste form into seawater. Measurement of pH and alkalinity content of the leachates were performed to assess the direction of ion transfer from the paste to the synthetic seawater or vice versa. Figure 3 shows the leachate pH and alkalinity results from one experimental run (mixed metal sample). This shows that the pH of the leachate (leaching solution after the extraction period) is initially much higher than that of the seawater leachant (initial leaching solution), indicating that hydroxide ions are being leached out of the cement into the seawater, as would be predicted by the dissolution of lime by chloride ions. The leachate pH's approach an equilibrium pH after several extractions. The equilibrium pH is slightly higher than that of the synthetic seawater leachant.

Leachate alkalinity data is also shown in Figure 3. Gran plot analyses and EDAX analyses indicate that there was a precipitation of calcium carbonate and magnesium hydroxide in the pores and on the surfaces of the paste particles. It is likely that carbonates are combining with dissolved calcium to form calcium carbonate structures such as calcite and aragonite. Some hydroxides may react with magnesium in the seawater and be precipitated as magnesium hydroxide or brucite. The precipitation of these materials was visually evidenced by a thick, white coating on the paste pieces. This resulted in a sealing of the pores which should lead to reduced metal leaching

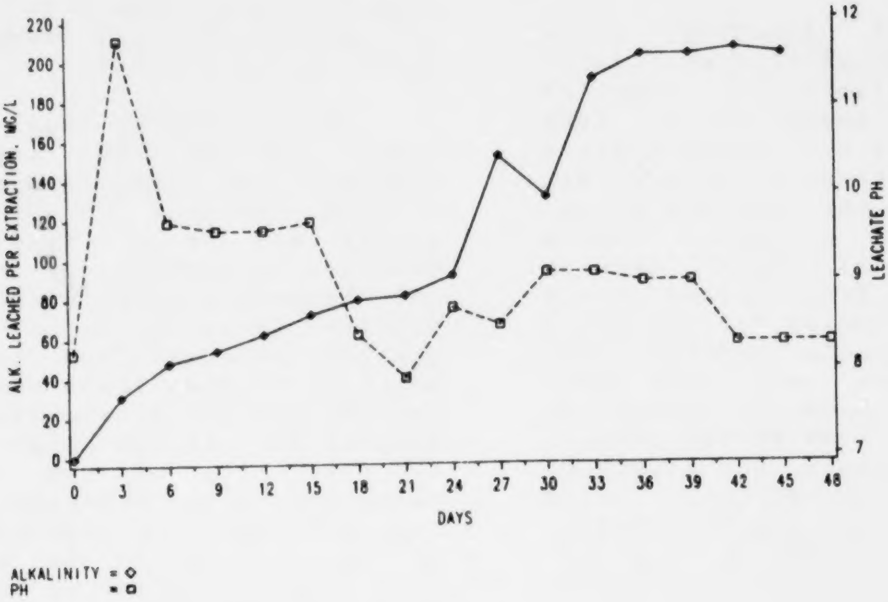


Figure 3. Leachate pH and alkalinity concentrations from stabilized/solidified wastes leached with seawater.

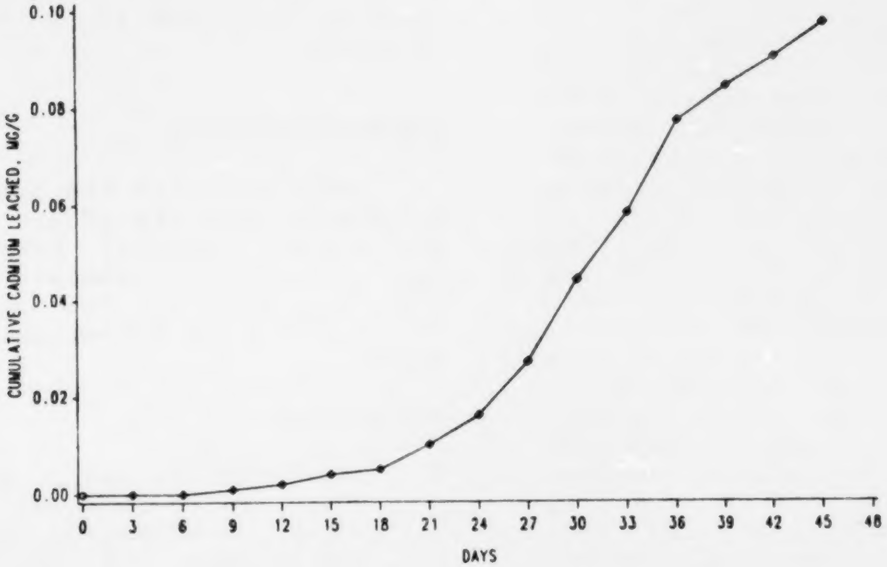


Figure 4. Cumulative cadmium leached from stabilized/solidified wastes cured for two years before leaching with seawater.

rates and reduced attack by chloride ions.

Metal leaching rates from solidified/stabilized wastes placed in seawater were extremely small. Even extraction and concentration of the leachate metals did not bring the lead and chromium up to detection limits (<1.0 ug/l). Only cadmium leaching from wastes which had been curing for two years was detectable and its concentrations were very low. After 50 days of leaching, less than 1.0% of the cadmium in the waste had leached. Wastes which had been curing for shorter periods before seawater immersion did not leach measurable quantities of cadmium.

Figure 4 shows the cumulative cadmium concentrations present in seawater leachates in one series of experiments with the two year old samples. LX values for cadmium in these wastes were over 15, indicating essentially complete immobility. It is postulated that cadmium leaching occurred only in these samples because they had been cured totally in an environment which precluded the formation of brucite, which would cause pore blocking and reduced metal leaching, and which encouraged the formation of ettringite, an expansive compound which causes cracking of the cement paste and thus increased leaching rates. Scanning electron microscopy of specimens placed in seawater shortly after formation showed that they had little or no ettringite formation, but did have extensive brucite deposits. Even in the old samples, though, cadmium leaching was minimal.

The results of this research indicate that marine disposal of solidified/stabilized inorganic hazardous wastes may be a feasible solution to much of our current hazardous waste disposal problem. Leaching rates are greatly reduced from those which occur when these wastes are exposed to groundwaters, largely due to the high pH and alkalinity of the seawater and to the presence of magnesium which precipitates in the waste pores as brucite. Ocean disposal of these wastes may be safer than terrestrial disposal. Research currently underway is investigating this using full-scale waste forms placed at several locations in the Gulf of Maine.

ACKNOWLEDGEMENTS

This research was funded by grants from the Office of Sea Grant, National Oceanic and Atmospheric Administration, and from the New Hampshire Office of Waste Management.

REFERENCES

1. Landreth, R. and J. Mahloch, 1977, Chemical Fixation of Wastes, Ind. Water Eng., Vol. 14, pp. 16-19.

2. Bishop, P. and D. Gress, 1986, Evaluation of the

Potential for Marine Disposal of Stabilized/Solidified Inorganic Hazardous Wastes, Office of Sea Grant Report, NOAA, 108 p.

3. El Korchi, T., K. Melchinger, B. Kolvites and D. Gress, 1986, The Effect of Heavy Metals and Organic Solvents on the Microstructure of Cement Stabilized Hazardous Waste, In: Proceedings of the Eighth International Conference on Cement Microscopy, Orlando, FL, pp.132-143.

4. Bishop, P. 1985, Development of a Dynamic Leaching Test for Stabilized/Solidified Hazardous Wastes, report submitted to New Hampshire Office of Waste Management, Concord, NH, 144 p.

5. Brown, T. and P. Bishop, 1985a, The Effect of Particle Size on the Leaching of Heavy Metals from Stabilized/Solidified Wastes, In: Proceedings of the International Conference on New Frontiers for Hazardous Waste Management, Pittsburgh, PA.

6. Bishop, P., 1986, Prediction of Heavy Metal Leaching Rates from Stabilized/Solidified Hazardous Wastes, In: Proceedings of the 18th Mid-Atlantic Industrial Waste Conference, Blacksburg, VA.

7. Brown, T. and P. Bishop, 1985b, Alkalinity Releases and the Leaching of Heavy Metals from Stabilized/Solidified Wastes, In: Proceedings of the 5th International Conference on Chemistry for the Protection of the Environment, Leuven, Belgium.

8. Shively, W., P. Bishop, T. Brown and D. Gress, 1986, Leaching Tests of Heavy Metals Solidified and Stabilized with Portland Cement, Journal Water Poll. Contr. Fed., Vol. 58, pp. 234-241.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

SOLUBLE SILICATES IN SOLIDIFICATION AND FIXATION TECHNOLOGY

Jesse R. Conner
Conner Technologies
Atlanta, GA 30319

ABSTRACT

Solidification and fixation systems based on, or incorporating, soluble silicates have been in commercial use since 1970 in the U.S. This technology has been successfully used for hazardous wastes, low-level nuclear wastes, municipal sludges and non-hazardous liquid wastes in at least several hundred projects or applications. Most commercially important solidification processes are based on or contain relatively insoluble silicates such as cement, flyash, clay and various kiln dusts. However, the reactions of soluble silicates such as sodium silicate are quite different. For practical purposes, these reactions make soluble silicates especially useful for two primary applications: fixation of dissolved metal ions, and rapid gelling of low solids slurries and sludges.

The ability of soluble silicates to form very stable, low solubility compounds with polyvalent metals is well proven and is the basis for one important use of this system. An equally important property of soluble silicates is their ability to produce stable gels of very high water content. This property is used in solidification technology to quickly gel low viscosity, low solids-content wastes so that all constituents are kept in homogeneous suspension in the gel while the mixture hardens to produce a physically and chemically stable solid. By using soluble silicates, chemical costs and volume and weight increases are minimized for these wastes.

INTRODUCTION

The history of chemical solidification and fixation (CFS) of industrial wastes dates back to about 1970 (2). Its roots go back to similar technology used for soil stabilization, grouting, mine backfilling and production of stabilized base courses for road construction. There was also earlier work done in the field of nuclear waste stabilization. Insoluble silicates in the form of Portland cement, flyash,

Preceding page blank

kiln dusts and clays were used in many of these processes, but the only recorded use of soluble silicates was in injection grouting of unstable soils.

When the use of soluble silicates was introduced for CFS treatment of wastes in 1970 (1), solidification of industrial residues was done primarily to make sludges and liquids physically more suitable for handling in landfills. Although CFS technology is now an accepted operation most workers in the field have little understanding of the chemistry of CFS processes.

PURPOSE

In the particular case of soluble silicate processes, there appears to be more misunderstanding and confusion than with the other major process types. This is due not only to the greater complexity of the process, but also because it is used for several distinct and different purposes. This paper discusses both the process chemistry and how it is interrelated to the various uses.

METAL FIXATION

The reactions of polyvalent metal salts in solution with soluble silicates have been studied extensively over many years (8). Nevertheless, the "insoluble" precipitates which result from such interactions are not well characterized, especially in most complex waste systems.

Reactions in Solution

Knowledge in this area is best summarized by Vail (8), who states "The precipitates formed by the reaction of the salts of heavy metals with alkaline silicates in dilute solution are not the result of the neat stoichiometric reactions describing the formation of crystalline silicates, but are the product of an interplay of forces which yield hydrous mixtures of varying composition and water content." These reaction products are, usually, non-crystalline and therefore very difficult to characterize structurally. They are most often described as hydrated metal ions associated with silica or silica gel. Iler (7) mentions "that many ions are held irreversibly on silica surfaces by forces still poorly understood in addition to ionic attraction" (4).

The composition and form of the metal "silicates" formed from metal ions and soluble silicates are functions of the conditions under which they are formed: temperature, concentration, addition rate, metal ion speciation, presence of other species, etc. For example, in dilute solutions, the species may remain in colloidal suspension, while at higher concentration or in the presence of other destabilizing conditions, it will precipitate (5). Metals are often present as soluble complexes or as negatively charged anions which should not bind to the silica surface. PH is very important for, as Iler (7) has pointed out, "silica suspended in a solution of most polyvalent metal salts begins to adsorb metal ions when the pH is raised to within 1-2 pH units below the pH at which the polyvalent metal hydroxide is precipitated." If the pH is not raised, the metal is not precipitated; if the pH of the system is already above this adsorption point, the metal may precipitate as the hydroxide instead. Different metals have different precipitability by soluble silicate solutions. According to Vail (8), the order in simple solutions, beginning with the most precipitable, is copper, zinc, manganese, cadmium, lead, nickel, silver, magnesium, calcium.

Real Systems

The above discussion deals only with some aspects of reactions in solution, and only with those between the metal species and the soluble silicate. With real wastes, the components may be present also as suspended solids or in immiscible liquid phases. Metals may already be speciated as relatively insoluble hydroxides or other solid phase compounds. Nearly always, cement or other solidification reactant is added to the system. These materials themselves often interact in complex ways with the metal species, as well as with the soluble silicate. If too little soluble silicate is added to the system, the reaction products which form will depend on which competing reactions are most successful, and also on the order of addition of the reactants. If an excess is added, unwanted leachable metal ion - silica complexes may form (5). The rate of addition, degree of agitation and temperature will also affect the nature of these reaction products, as they do in many other chemical systems.

The aspect of soluble silicate fixation of metals which seems most confusing to workers in the field involves the speciation of the cation before the silicate is introduced into the system. Most wastes which are treated by CFS are sludges, filter cakes and other residues from waste water treatment systems. The metals have been precipitated with lime or other sources of hydroxyl ion, or with other agents such as sulfide, to produce metal hydroxides, sulfides, etc. which have low solubility under the conditions of precipitation, usually in the pH range of 7 to 10 and a dilute water medium. In this state, there is little reaction between the metal species and the soluble silicate. If the metal hydroxide is more soluble than the silicate, there may be gradual re-speciation of the hydroxide at the particle surface, but total re-speciation would not be expected to occur except over a very long period of time. Furthermore, the soluble silicate will not be available as such for long, because it will react with other components of the CFS system (discussed below). The immediate result is the original mixture of metal compounds dispersed in a cementitious matrix.

Leachability of this solid will be determined by a number of factors, including solubility of the metal compounds, adsorption, diffusion, ion exchange, etc. It is also determined by the permeability of the monolith, which in turn is a function of pore structure and the amount of water present in the waste (3). Here, the primary function of the soluble silicate (other than for the gelation/solidification reactions) is to reduce permeability. It does this by forming precipitates in the matrix which block pores (5), reducing the effective pore volume and slowing the movement of any mobile species through the matrix into the environment. This effect may be responsible for the reduced leachability of species which would not be expected to react with soluble silicates: monovalent cations, anions and organics (2). It also accounts for the fact that monoliths produced by CFS usually show higher levels of leachability when subjected to mechanical degradation, either naturally or during leaching test procedures. Grinding or crushing the monolith increases the surface area in contact with the leaching medium, thereby reducing the contribution of impermeability produced by the CFS process.

The problem of speciation is avoided when the metal species is in solution. Unless it is complexed in soluble, stable form, the metal can usually be precipitated from solution as a silicate which exhibits low solubility through a wide pH range. (6) This is especially important for the heavy metals of environmental interest which exhibit amphoteric behavior such as chromium, zinc, nickel, copper, etc. The hydroxides of these metals exhibit minimum solubility through a narrow pH range, usually in the area of pH 7.5 to 9; it increases rapidly above pH 10. Because most CFS systems are quite alkaline, usually above pH 11, the solubility of the metal species in the CFS-treated waste may actually be higher than in the original, untreated sludge.

This difficulty tends to be exacerbated with increased surface area. While the soluble silicate can respeciate the metal hydroxide as the latter dissolves, it usually will not be available because it will have been used up in other reactions with matrix-forming agents. There are three solutions to this problem: (1) reduce permeability, (2) add a fixant other than silicate which remains available in the matrix as needed, or (3) pretreat the waste by reducing pH to dissolve the metal hydroxide, then re-speciate as silicate.

Another set of complexities is introduced by the way in which industrial metal hydroxide or sulfide residues have been handled in the past. Typically, these materials are stored in lagoons where other residues or waste products may be added. Some of the added residues may be the result of water treatment systems - for example, biological processes for organic wastes - while others may be concentrated, untreated process wastes. Frequently, water immiscible organics such as oily lubricants will be carried along with the waste streams into the lagoon. Thus, an extremely complex mixture forms, and further reactions among the various wastes and as a result of weathering and aging may occur. Little has been documented about the nature of these reactions, but their effects on physical and chemical characteristics of the mixed wastes have been observed.

The additional components may also interfere with otherwise possible reactions between metal species and soluble silicates, or will themselves precipitate the silicate from solution before it can achieve either of its purposes: fixation or gelation/solidification. Oily constituents, for example, may coat reactive particles, preventing reaction with soluble silicate. When the oil is removed as a first step in the EPA Oily Waste Extraction Procedure, the unreacted material will then leach at higher than expected rates.

Soluble silicate CFS systems can reduce the leachability (as measured by the EPA Extraction Procedure) of heavy metals to levels below 0.1 mg./l. in most wastes. Often, much lower levels can be achieved. While the reduction in leachability obtained is usually dependent on the leaching test used, tests considered most severe (such as the California WET) do not always give the highest leachability with every metal. Unfortunately, we cannot predict the leachability in these systems from theoretical models, which is not surprising in view of the complexities described above.

GELATION AND SOLIDIFICATION

Soluble silicates are one of the oldest classes of industrial chemicals known. They have been used for myriad purposes and their reactions and uses are well described in the literature (8). There are many possible silicates which can be used and a number of reactants or setting agents. However, the overriding consideration in formulating any system for CFS use has been cost. In view of this and other factors, the most commercially important system to date has been that which uses Portland cement, Type 1, and a 38% solution of sodium silicate (silica to sodium oxide ratio of 3.22). The latter is a syrupy liquid with density of 11.6 lb/gal and pH of 11.3; it is commonly known as "water glass." These two chemicals are the most widely used in their respective categories, and are the lowest priced grades. While other cements and silicates have been proposed, and several used, for specific purposes, this paper will discuss only the Portland cement - sodium silicate solution (PCSS) system.

Each of the two materials used in this system is capable of forming a solid, cemented mass under the right conditions. This property of Portland cement (PC) is obvious, and a number of CFS processes use it alone or in various other combinations. (Cote (3) gives an excellent discussion of this subject) Sodium silicate solution (SS) can also act to form a solid, with components of the waste itself, when reactive species such as polyvalent metal ions are present.

In the PCSS system, the PC is often referred to as the setting agent for the SS. At the same time, SS is used as an accelerator or anti-inhibitor for the setting of PC, and the hardening which takes place as the solidified waste cures is due primarily to the PC. There is no contradiction in this; both processes take place at different times during solidification, although there is no sharp delineation between them and they may overlap on the time scale. The chemistry of the system is more easily understood by examining the reasons (in addition to fixation of metals) for using SS in solidification work: (1) to quickly gel low solids wastes, and (2) to aid in the PC hardening process.

Gelation

Most industrial waste streams, especially those stored in lagoons, contain large amounts of water. When the PCSS process was first introduced, most wastes had solids contents of less than 20%. Today, with the emphasis on volume reduction, wastes are usually dewatered where possible to produce semi-solid "cakes", but there are still many instances where dewatering is not feasible. For example, in remedial action work solidification is commonly practiced on the lagoon waste without any pretreatment.

One difficulty with solidification of these low solids, low viscosity wastes is that they settle rapidly when not agitated. Since most CFS processes solidify slowly - over a period of hours or days in most cases - a contaminated watery layer remains on top of the hardening mass. This is usually undesirable. One of the reasons for developing the PCSS process was to eliminate this effect by quickly gelling the mass, increasing viscosity to the point where settling could not occur. As a result, all constituents are kept in a homogeneous suspension in the gel while the mixture hardens to a true solid. The alternative is to add large amounts of inexpensive ingredients which act primarily as fillers, artificially increasing the solids content and viscosity of the waste so that it cannot settle while it hardens.

The gelling ability of SS is unique, and should not be confused with various gelling or thickening agents, usually organic gums or polymers, which act by physical means only. In the PCSS system, gelation occurs chemically by reaction of the SS with free calcium hydroxide present in the PC, or produced by hydration when PC is mixed with water. SS is not a simple solution, because it contains both polymeric silicates and colloidal silica. These species interact with divalent ions such as calcium to form a silica/silicate gel which holds all of the available system water, as well as the non-dissolved solids, suspended in a non-mobile state (7,8).

The initial gel is quite delicate, and forms properly under only the right conditions of concentration, addition rate, temperature, etc. Addition of SS to a concentrated solution of polyvalent metal ion will result in a hard, dense precipitate, not a gel. Too little metal ion will result in slow gel formation, or none at all. To be effective, the gel must immobilize the suspended solids, including the PC, within a period of several seconds to several minutes, depending on the waste and the mechanical aspects of the CFS system.

An uncommon property of the PCSS system is that PC provides just the right amount of calcium ion in solution at any given time. It does this by hydration of the cement's components, which occurs slowly enough so that hard precipitation of the silicate does not take place. As the calcium ion from the PC is used up, more is generated by hydration to further react with the remaining SS, strengthening the gel. At the same time, the PC begins its own series of reactions which first produce setting and then hardening. There is competition for the calcium ion between the SS and hydrosilicate residues on the cement grains. Since the PC setting reaction is substantially slower than the SS gel formation, the latter occurs at the expense of the former. As the SS is used up, the calcium ion becomes available to enter into the PC's own gel reactions which result in the PC setting phase. The PC then continues to harden through its complex set of reactions which continue almost indefinitely (3).

Obviously, the presence of metal ions from the waste itself, as well as many other common waste components, will affect the gelling properties of SS in this system. One common example is pH; acid wastes will precipitate the SS before the gel can be formed. It is beyond the scope of this paper to examine all of the various problems which are encountered with different waste streams. What is surprising is that the system works so well with so many and varied waste types, given the complexity and sensitivity of the reactions which must occur.

PC Hardening

Many potential waste constituents can act as retarders or accelerators in the setting of PC. The presence of accelerators is not usually a problem, but retarders can slow or even prevent the hydration of the calcium silicate components of PC. There are compounds or ions which form precipitates on the surface of the cement grains, for example, gypsum and salts of heavy metals such as zinc, copper and lead. Another category of retarders adsorb on the cement grains, or coat them so that reaction with water is prevented; these are exemplified by fine particulates such as silt and clay, and by organics such as oil and algae.

SS has been used as an accelerator and anti-inhibitor for concrete, and has the same function in PC-based CFS systems. In the case of the precipitant type retarders such as heavy metals, SS probably works by removing the metal from solution before it can precipitate on the cement grains. With retarders that operate by coating the grains, SS may function as a surfactant, emulsifying oils and flocculating fine particulates so that they remain suspended in the water phase. In any case, SS has been useful in many instances for this purpose rather than as a fixant or gellant.

SUMMARY

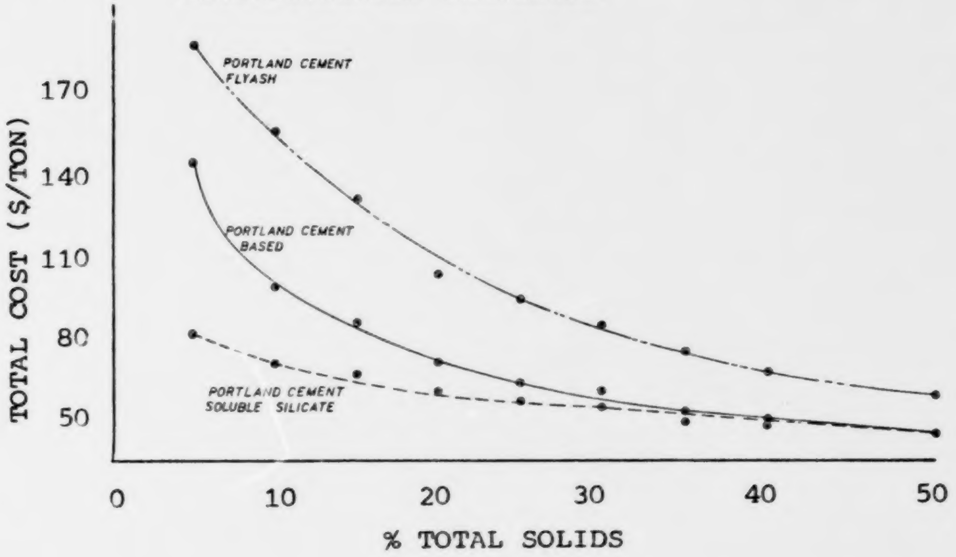
Soluble silicates, have been widely used in CFS work because of several important properties: their ability to fix metals, to quickly gel low-solids wastes, and to prevent inhibition of cement-based systems.

The gelation function of the PCSS system often makes it the process of choice for low-solids wastes. This is shown graphically in Figure 1, where the total cost (solidification plus landfill) is plotted against % solids for three processes: PCSS, PC alone (plus minor additives) and PC plus flyash. The data used here comes from test work and commercial solidification projects on real wastes over a period of about 15 years; all costs are in 1984 dollars. For this analysis, the following cost assumptions were used: PC - $70/ton; SS - $140/ton; flyash - $13/ton; industrial landfill - $40/ton. Transportation costs were not included in this analysis.

At 5% solids, the PCSS process costs about half that of PC/flyash and about 60% that of PC alone. At 20% solids, the numbers are 63% and 87%, respectively. At high solids (40 - 50%), the cost of the PCSS and PC processes are nearly identical, and both are about 75% that of PC/flyash.

The explanation for this, of course, is that the gelling ability of SS allows the use of smaller quantities of CFS chemicals, even though they have higher unit costs. This results in lower weight and volume increase in the final solid product. For example, the weight increase due to CFS treatment for a 20% solids sludge was only 20% for PCSS, compared to 33% for PC and 98% for PC/flyash. As landfill costs continue to escalate, minimizing weight and volume increase will become even more important.

Figure 1. Total Cost As A Function of Total Solids For Various Solidification Processes



REFERENCES

1. Conner, J.R., 1974, Method of Making Wastes Non-polluting and Disposable, U.S. Patent No. 3,837,872.

2. Conner, J.R., 1974, Ultimate Disposal of Liquid Wastes by Chemical Fixation, Proc. 29th Ann. Purdue Indus. Waste Conf., Purdue University.

3. Cote, P., 1986, Contaminant Leaching from Cement-Based Waste Forms Under Acidic Conditions, PhD Dissertation, McMaster Univ., Canada.

4. Falcone, J.S., 1982, Soluble Silicates, Reinhold, New York, NY, Vol. 1, pp 151-158, 200-254.

5. Falcone, J.S., 1986, Private Communication.

6. Gowman, L.P., 1975, Chemical Stability of Metal Silicates vs Metal Hydroxides in Ground Water Conditions, Proc. 2nd Nat'l Conf. on Complete Water Reuse, May, Chicago, Il.

7. Iler, R.K., 1979, The Chemistry of Silica, Wiley, New York, NY, Chapter 6.

8. Vail, J.G., 1952, Soluble Silicates, Reinhold, New York, NY, Vol. 1, pp 151-158, 200-254.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

IN SITU VITRIFICATION - AN INNOVATIVE THERMAL TREATMENT TECHNOLOGY

V. F. FitzPatrick
C. L. Timmerman
J. L. Buelt

Pacific Northwest Laboratory
Richland, Washington

INTRODUCTION

As management of hazardous materials gains increased attention in the United States, new and more effective technologies are being sought to immobilize and/or destroy the wastes, either in situ for previously disposed wastes or at the waste generation site. The new Hazardous and Solid Waste Amendments (HSWA) 1984 and the Superfund Amendments and Reauthorization Act (SARA) 1986, combined with proposed rule making by the U.S. Environmental Protection Agency (EPA), is making landfill disposal very costly and is moving in a direction that will severely limit future land disposal. Further, the extended liability associated with future environmental impairment provides a significant corporate incentive to dispose and delist wastes within the plant or waste site boundary.

Pacific Northwest Laboratory (PNL) is developing a remedial action process for contaminated soils that is potentially significant in its application to these concerns. Although the process was initially developed to provide enhanced isolation to previously disposed radioactive wastes, recent tests have shown that many hazardous chemical wastes are also destroyed or immobilized as a result of the treatment. The process, in situ vitrification (ISV), was originally developed for the U.S. Department of Energy (DOE) and is more recently being adapted for selected commercial clients for hazardous wastes.

In situ vitrification is a thermal treatment process that converts contaminated soil into a chemically inert, stable glass and crystalline product. Figure 1 illustrates how the process operates. A square array of four electrodes are inserted into the ground to the desired treatment depth. Because the soil is not electrically conductive once the moisture has been driven off, a conductive mixture of flaked graphite and glass frit is placed among the electrodes to act as the starter path. An electrical potential is applied to the electrodes, which establishes an electrical current in the starter path. The resultant power heats the starter path and surrounding soil up to 3600°F, well above the initial melting temperature or fusion temperature of soils. The normal fusion temperature of soil ranges between 2000 and 2500°F. The graphite starter path is eventually consumed by oxidation, and the current is transferred to the molten soil, which is now electrically conductive. As the vitrified zone grows, it incorporates nonvolatile elements and destroys organic components by pyrolysis. The pyrolyzed byproducts migrate to the surface of the vitrified zone, where they combust in the presence of oxygen. A hood placed over the processing area provides confinement for the combustion gases, and the gases are drawn into the off-gas treatment system.

Preceding page blank

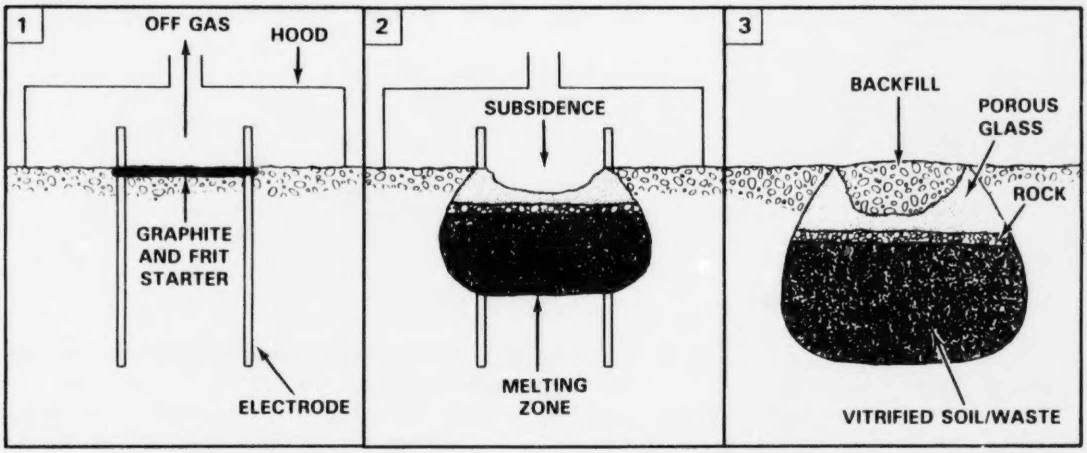


FIGURE 1. The In Situ Vitrification Process

Pacific Northwest Laboratory began developing ISV technology in late 1980 under the support of DOE. Since then, numerous experimental tests with varying conditions and waste types have been conducted (Buelt and Carter 1986a, 1986b; Timmerman and Oma 1984). Table 1 describes the different scales of test units that PNL used in developing the technology. The successful results of the 45 bench-, engineering-, and pilot-scale tests have proven the feasibility of the process. Also, economic studies have indicated that tremendous economies of scale are attainable with the ISV process (Oma et al. 1983). This finding led to the commitment to design, fabricate, and test a large-scale prototype. Its successful testing has demonstrated the field utility of the large-scale unit and has proven the initial economic projections.

TABLE 1. In Situ Vitrification Test System Characteristics

System, Scale	Power, kW	Electrode Spacing, ft	Vitrified Mass per Setting	Number of Tests
Bench	10	0.36	2 to 5 lb	5
Engineering	30	0.75 to 1.2	0.05 to 1.0 ton	26
Pilot	500	4.0	10 to 50 ton	15
Large	3750	11.5 to 18.0	400 to 800 ton	5

This paper describes the large-scale ISV system, discusses its capabilities, and summarizes the results of testing to date. Pacific Northwest Laboratory recognizes that ISV is not the solution to all hazardous waste management problems. But judiciously applied, ISV can offer technical and economic improvements to state-of-the-art remedial action technology. With an understanding of the process design and functions, the waste manager can make sound judgments about the applicability of ISV to site-specific disposal problems.

PROCESS AND OPERATION DESCRIPTION

As the melt grows downward and outward, power is maintained at sufficient levels to overcome the heat losses from the surface and to the surrounding soil. Generally, the melt grows outward to about 50% of the spacing of the electrodes. Therefore, if the electrode spacing is 18 ft, a melt width of about 28 ft would be observed under nominal conditions. The molten zone is roughly a square with slightly rounded corners, a shape that reflects the higher power density around the electrodes.

As the melt grows in size, the resistance of the melt decreases, making it necessary to periodically adjust the ratio between the voltage and the current to maintain operation at constant power. This is done by adjusting the tap position on the primary power supply to the electrodes. There are 14 effective taps that permit adjusting the voltage from a maximum of 4000 V to a minimum of 400 V per phase and the current from a minimum of 400 A to a maximum of 4000 A per phase. Operations follow the power equation

$$P = I^2 \times R \tag{1}$$

where P is power, I is current, and R is resistance.

The large-scale process equipment for ISV is depicted in Figure 2. The process immobilizes contaminated soil and isolates it from the surrounding environment. Controlled electrical power is distributed to the electrodes, and special equipment contains and treats the gaseous effluents. The process equipment required to perform these functions is divided into five major subsystems: 1) electrical power supply, 2) off-gas hood, 3) off-gas treatment, 4) off-gas support, and 5) process control.

Except for the off-gas hood, all components are contained in two transportable trailers (Figure 3): an off-gas and process control trailer, and a support trailer. These trailers are mounted on wheels sufficient for a move to any site over a compacted ground surface. The off-gas hood and off-gas line, which are installed on the site for collection of the gaseous effluents, are dismantled and placed on a flatbed trailer for transport between the sites to be treated. The effluents exhausted from the hood are cooled and treated in the off-gas treatment system. The entire process is monitored and controlled from the process control trailer.

The off-gas trailer is the most complex and expensive of the two trailers. The off-gas treatment system cools, scrubs, sorbs organics, and filters the gaseous effluents exhausted from the hood. The primary components include a gas cooler, a wet scrubber system (tandem nozzle scrubber and quencher), a heat exchanger, process scrub tank, scrub solution pump, a condenser, two mist eliminators (vane separators), a heater, a charcoal filter assembly, and a blower system.

A major element of the off-gas support system is the glycol cooling system, which is mounted on the support trailer. This system interfaces with

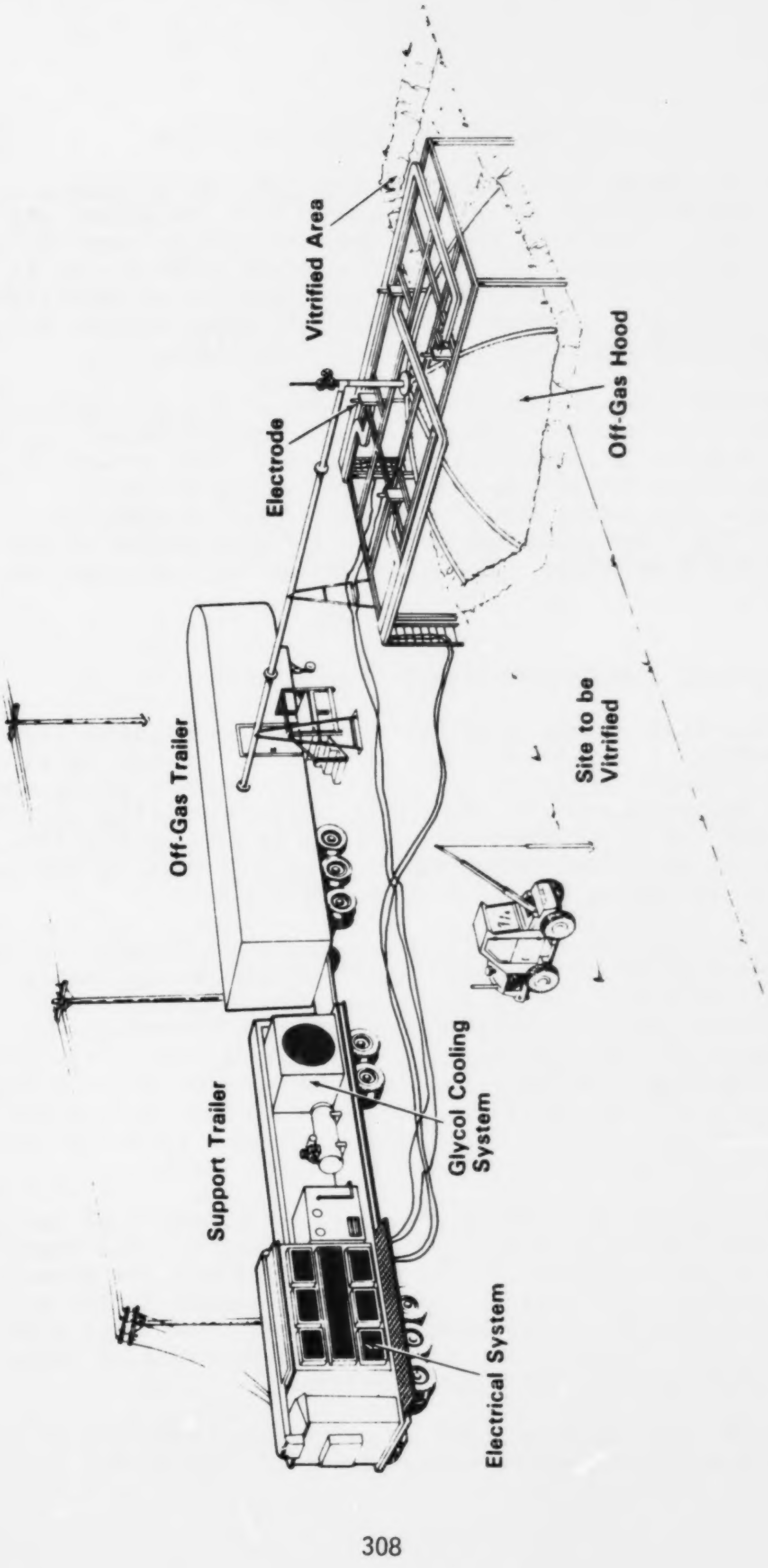

Electrical System
Support Trailer
Glycol Cooling System
Off-Gas Trailer
Site to be Vitrified
Electrode
Off-Gas Hood
Vitrified Area

Figure 2. Setup for In Situ Vitrification

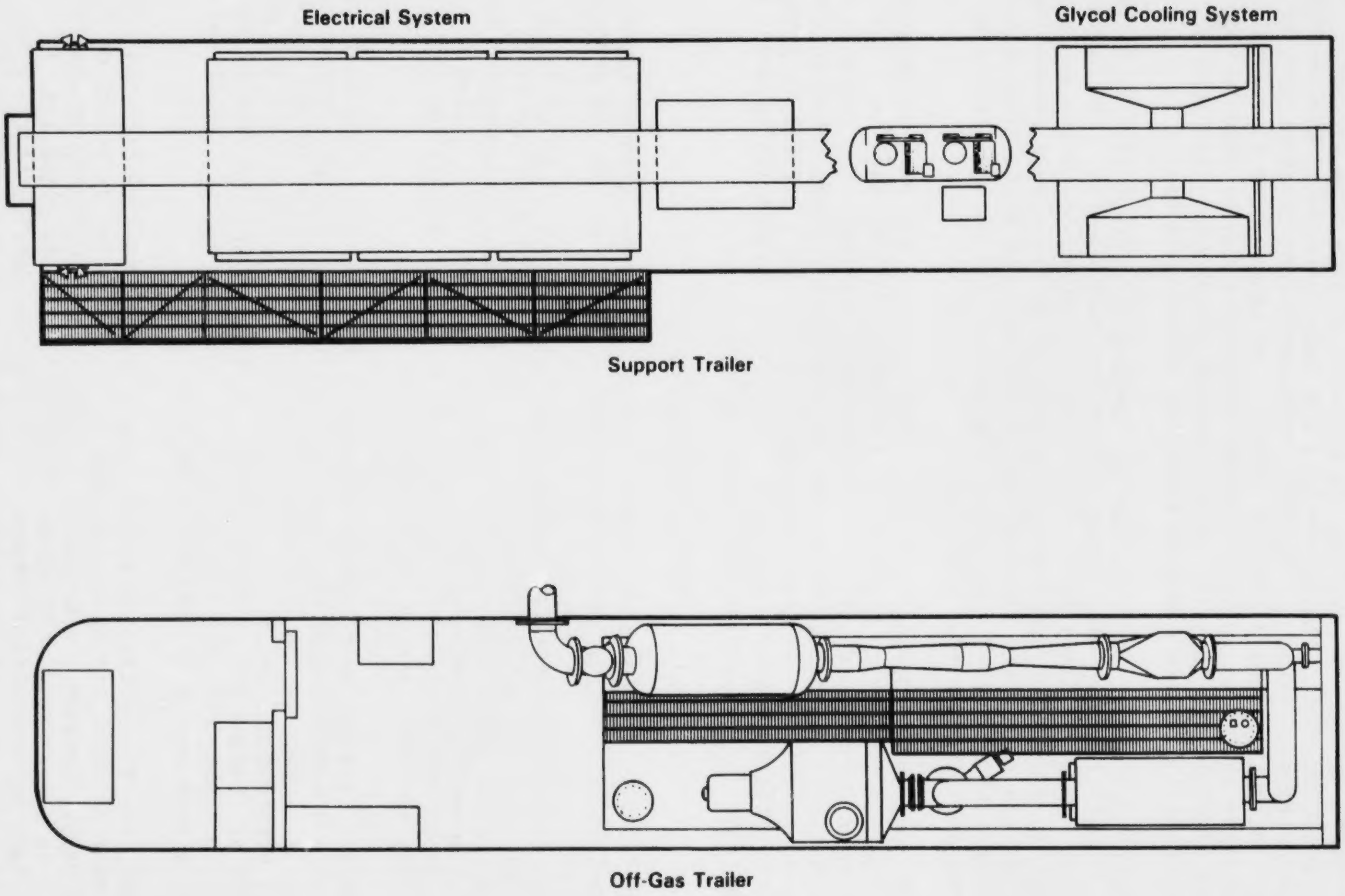

Electrical System
Glycol Cooling System
Support Trailer
Off-Gas Trailer

FIGURE 3. Process Trailers for the Large-Scale In Situ Vitrification Unit

the scrub solution and extracts the thermal energy that builds up in the off-gas treatment system from cooling the combustion gases from the hood. The heat is rejected to the atmosphere in a fin tube, air-cooled heat exchanger. The entire process system is therefore self-sufficient in terms of site services, except for the electrical supply. In cases where electrical supply is remote and costly to bring in, diesel generators can be used to supply the required electricity. Details of the large-scale process equipment and the process capabilities are found in Buelt and Carter (1986b).

The normal processing rate for the large-scale system is 4 to 5 ton/hr, a rate competitive with many other remediation technologies. The average processing operation lasts about 150 to 200 hr, depending on the depth and electrode spacing. For processing to depths of 50 ft, single processing operations can run in the range of 300 to 400 hr. The production rate will remain constant at 4 to 5 tons during the entire time period, resulting in a vitrified mass greater than 1000 tons.

For routine operations on a site, both trailers are coupled together and moved from one processing position to another by pulling them as a unit. The hood is moved from one position to another with a crane. The crane is also used to assist in coupling and uncoupling the off-gas lines. Moving from one processing position to another takes about 16 hr; thus, a relatively high operating efficiency can be achieved. This 16-hr interim for movement also provides time for performing routine maintenance.

PRODUCT CHARACTERISTICS

The ability of the waste form to retain the encapsulated or incorporated heavy metals is of prime importance to the usefulness of the ISV process.

The vitrified waste form has been subjected to a variety of leach tests, including EPA's Extraction Procedure Toxicity Test (EP Tox) and Toxic Characteristics Leach Test (TCLP). These tests show a uniformly low leach rate for heavy metals of about 5×10^{-5} $g/cm^2/day$ or lower. Based on limited tests, we can assume that the vitrified material can be delisted under the provisions of either the EP Tox or the TCLP.

Another indication of the durability of the ISV waste form is found in a study of the weathering of obsidian, a glasslike material physically and chemically similar to the ISV waste form (Ewing and Hocker 1979). In the natural environment, obsidian has a hydration rate constant of 1 μm^2 to 20 μm^2/1000 yr (Larsen and Langford 1978). A linear hydration rate of 10 μm^2 produces a highly conservative estimate of a <<1 mm hydrated depth for the ISV waste form over a 10,000-year time span.

Data for the release of sodium from vitrified Hanford Site soil during a leach test at 194°F are available (Oma et al. 1983) for durations of 7, 14, and 28 days. Because the sodium is soluble in the leachate, its normalized release is a measure of the extent of hydration of the glass and, in particular, its normalized release divided by the density of the glass is the depth of hydration. If the glass is assumed to hydrate according to the same parabolic rate law as has been found for obsidian, then the square of the depth of hydration divided by the duration of the test should be constant. Using the data in Oma et al. (1983), the result of this calculation increases between the 7- and 14-day data, but then is constant between the 14- and 28-day data. Taking this final value and using the density of the glass, the hydration rate at 194°F appears to be about 2 μm^2/yr. In the literature on field studies of obsidian hydration, the rate is found to obey an Arrhenius relation with an activation energy of 20 kcal/mole. Applying this to the ISV glass hydration, we can predict rates of 5 μm^2/1000 yr at 77°F (e.g., for glass exposed to the air) and 1 μm^2/1000 yr at 50°F (e.g., for glass buried underground). These values are comparable to those found for obsidian hydration rates in the field for similar average weathering temperatures.

The long-term stability of obsidian in nature is controlled by three mechanisms (Ewing and Hocker 1979): alteration (weathering), devitrification (recrystalization), and hydration (water absorption) (Larsen and Langford 1978). A review of the literature indicates that the usual controlling mechanism is devitrification. Studies of the mean age of natural glasses indicate that obsidian has a mean life of about 18 million years (Ewing and Hocker 1979). Considering the similarity of the ISV waste form to obsidian, we can reasonably postulate that the mean life of the vitrified material would be on the order of 1 million years.

The ISV waste form is a glass with an atomic structure that is random, rather than the highly structured nature of a crystalline material. This leads to another benefit: the fracture mechanism is conchoidal; i.e., the waste form is not subject to significant damage by freeze/thaw mechanisms that can accelerate natural degradation.

ECONOMIC ANALYSIS

The economics of the process have been examined under various conditions representing typical conditions that might be encountered throughout the United States. While the methodology for developing ISV cost estimates was developed and reported (Oma et al. 1983) before the design, fabrication, and testing of the large-scale system, the approach is still considered valid. The two key assumptions in the initial economic projections were that 1) the system could be operated with two people per shift, and 2) the system could be moved from one processing area to another processing area in less than 24 hr. Both of these assumptions have been proven correct (Buelt and Carter 1986a, Buelt et al. 1986).

Highlights of the cost estimate technique used for the initial cost projections are summarized here; details can be obtained from the original reference (Oma et al. 1983). The cost estimate is divided into five main categories: 1) site preparation, 2) equipment or capital recovery, 3) operations and labor, 4) electrode material, and 5) electrical power. The two factors that most significantly affect total cost are the amount of moisture in the soil and the cost of electricity. The amount of moisture directly affects operational time and, therefore, has a direct bearing on the operations and labor costs. The electrical energy equivalent of the heat of vaporization for the moisture in the soil must be supplied and the water boiled off before vitrification can proceed. The cost of electrical power also has a direct effect on the operational costs. Equipment or capital recovery costs and electrode costs are significant; however, they are treated as constants. Site costs are based on nominal amounts of civil work that must be performed, which include acquiring and placing clean backfill in the subsidence zone.

Equipment or capital recovery costs include the ISV system and the necessary support equipment, such as a front loader and crane for earth-moving operations and moving the hood and trailers, respectively. There is also a nominal allowance for extending existing power lines and installing a substation. All equipment is assumed to have a 10-yr life. The sum of the equipment costs is multiplied by a 20% capital recovery factor and added in as a unitized cost factor.

Operations and labor costs consist of the labor and materials for those activities that must be performed to support normal operations. These activities include labor time for the two operators required to operate the system. System operation is calculated on the basis of 24-hr continuous operations. Other support activities include digging the holes and placing the electrodes, moving the trailers and hood from one processing position to another, and performing routine maintenance operations when the system is being moved. Also included are costs for placing the starter material, and connecting, disconnecting, and testing the electrodes. The operational cost also includes an allowance for secondary waste disposal (i.e., treating and/or disposing the scrub solution once per week).

Electrode costs are for the purchase of electrode materials, which are used only once, assuming that the electrodes are left in the melt. For operations in a chemically hazardous environment, the electrodes can be retrieved and sold for salvage value, which is about 20% of the original cost. For operations with a process sludge where significant decomposition of the sludge occurs, there is a potential for electrode reuse; however, estimating electrode recovery values that are higher than the salvage value at this time is not conservative planning.

These cost factors have been calculated and plotted in graphical form (Figure 4). The maximum cost for all three cases occurs at an electrical rate of $.0825/kWhr. At local electrical rates that are higher than this value, the use of portable diesel generator power is recommended. Whether the units are rented or purchased depends on the length of the remediation operation and business decisions concerning future operations. The flat rate can also be used for planning for sites where local electrical power is unavailable and bringing in a power line would be very expensive. The case for process sludges was included to cover those situations where consolidation and immobilization at an active plant site was the primary objective. This could be important to the typical owner generator who has old sludge surface impoundments that must be closed and the owner/generator does not want to incur the long term liability associated with shipping to a land fill.

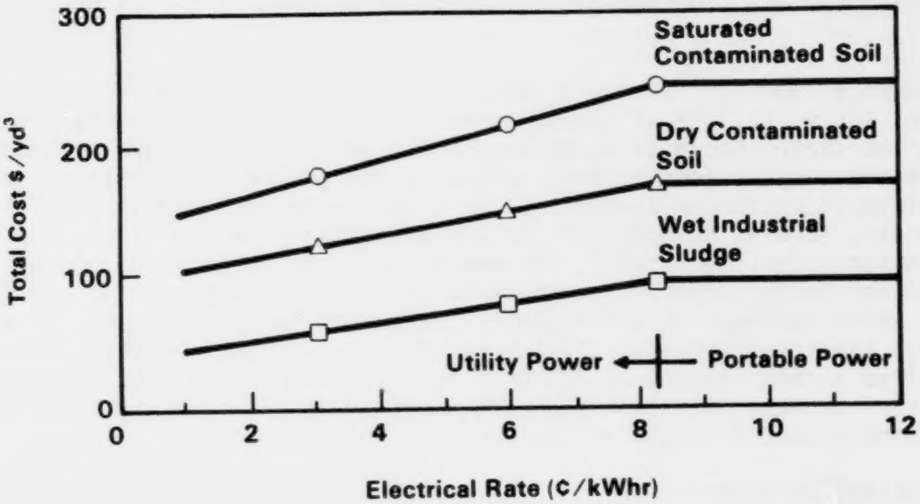


FIGURE 4. Cost of In Situ Vitrification Applications

PROCESS PERFORMANCE

The discussion on process performance is divided into two sections: 1) experience with hazardous wastes and 2) applications considerations. The discussion will focus on the overall treatment efficiency (i.e., the retention and/or destruction in the melt, and the capture and removal of the material released from the melt by the off-gas system). The sum of the two functions represents the overall system Destruction Removal Efficiency (DRE).

HAZARDOUS WASTE EXPERIENCE

The results of the process performance testing with hazardous materials are subdivided into two categories: metals and organics.

Metals

During the processing operations with ISV, metals are either dissolved in the glass or incorporated in the vitreous matrix. The three factors that have the largest effect on retention are burial depth, solubility, and vapor pressure. Burial depth has a direct function on retention, increasing the amount of retention with increased burial depth. Metals are retained in the melt as a direct function of the solubility and inversely proportional to their vapor pressure.

The measure of the material retained in the melt is the retention factor:

$$\text{Retention Factor} = RF = [A]i/[A]e \qquad (2)$$

where [A]i is the concentration of the element A initially present and [A]e is the concentration of element A exiting the component. This terminology is used for the retention in the melt as well as the retention in the off-gas treatment system. The retention factor is the inverse of the quantity [1-DRE].

When estimating retention factors for metals in the melt or off-gas system, the solubility of the metal in the glass and also the likely oxidation state should be considered. The melt is very reducing in nature, so the most likely form of most metals is either the pure state or the lowest oxidation state that will accommodate a stable oxide. Data from other glass processes, such as ceramic melters, is not considered a reliable source in estimating retention factors, because of the difference in reducing conditions in the glass. Ruthenium in an oxidizing environment can form RuO_3, which sublimes at about 1800°F and causes serious problems in melter off-gas treatment systems. In the pilot-scale radioactive test, ruthenium exhibited a retention of 99.82% or a retention factor of 550. The enhanced retention because of oxidization state and solubility, is important when assessing potential applications to traditionally volatile metals.

Retention factors measured in large-scale testing are shown for both the melt and the off-gas treatment system (Table 2). These data are sufficient so that an inference can be made to the retention of other hazardous metals. Results for large-scale testing show that retention continues to increase with increasing depth. An order of magnitude increase in retention was observed when the depth was increased from 3 to 16 ft (Buelt and Carter 1986a). The presence of combustibles can provide a path to the surface by entraining the metals in the combustion product or pyrolytic gases, decreasing the retention fraction. The closer to the surface, the more likely the entrained material will not be scrubbed out by the molten glass and recaptured. Even the decomposition of nitrates can provide an elution path if the reaction occurs near the surface.

TABLE 2. Retention Factors of Metals

Type of Metal	Soil	Off Gas	Combination
Particulates			
Sr, Pu, U, La, Nd	10^4 to 10^5	10^5	10^9 to 10^{10}
Semi-Volatiles			
Co, Cs, Sb, Ni, Mo	10^2	10^4	10^6
Volatiles			
Cd, Pb	3 to 30	10^4	~10^5

Organics

During processing, organics that are contacted by the vitrifous material are destroyed by pyrolysis. The pyrolytic gases move upward through the melt and combust when contacted by the oxygen atmosphere in the hood. The data base for processing organics has been limited to selected organics in containers, PCBs, dioxins (2,3,7,8 TCDD), and organics associated with electroplating wastes. As the ISV process gains additional acceptance as a remediation tool, the data base will grow, through feasibility tests, field demonstrations, and actual remediation applications.

Combustible testing with organics has included up to 110 lb of solid combustibles and 50 lb of liquid organic in a single pilot-scale experiment. The materials were packaged in a container such as what might be found in a solid-waste burial ground. Chromatographic, sample bomb, and mass spectrometric analyses of the effluent from both the hood and the exhaust stack showed less than 5 x 10^{-3} vol% release for light hydrocarbons during peak combustion periods. This level of release indicates nearly complete pyrolysis and combustion (FitzPatrick et al. 1984). A limited number of experiments have been conducted to define the pressure rise and rate of release associated with organics in sealed containers. Theoretical calculations predicted that the internal pressures would be several hundred psi, and that the pyrolized material would produce a transient pressure wave that would move through the melt in a few seconds. The tests were performed using the engineering-scale system; the sealed containers were lecture bottles, equipped with pressure sensors. The maximum pressure observed was 32 psig; the pressure attenuated over a period of 1-1/2 min. These data indicate that the metal softened as the vitrified zone approached the sealed container and that the intrusion of the glass was slower than the theoretical maximum rate. This could be a scaling effect, related to the relatively high viscosity of the glass. Intrusion into a buried 55-gal drum is expected to be very rapid. The organics in the containers were completely destroyed (DREs >99.99%).

An engineering-scale test was conducted using soils contaminated with 500 ppm of PCBs. The data from the test showed that the process destruction was slightly greater than 99.9%. The small amount of material released to the off-gas system was effectively removed, yielding an overall system DRE of >99.9999%. Analysis of the vitrified block showed that there were no residual PCBs; considering the processing temperature, the data are reasonable. The soil adjacent to the vitrified area was examined for PCBs; limited quantities were detected (0.7 ppm of PCBs). These data indicate that the vitrification rate is greater than the PCB diffusion rate and that migration away from the vitrification zone during processing is not a significant concern. The overall results were sufficiently promising that a pilot-scale test has been authorized. The scope of this test will be 1000 ppm PCB-contaminated soil and performed in accordance with a Toxic Substances Control Act (TSCA) permit issued for EPA Headquarters.

A bench-scale test was conducted on a soil contaminated with dioxin (2,3,7,8 TCDD). The initial results show that an overall system DRE of

99.99999% was obtained. No dioxins or furans were detected in the off-gas emissions during the test.

Engineering-scale tests on electroplating wastes have shown that the destruction efficiency for contaminated soils is >97% for the process even when the contaminated soil is not covered with a layer of clean soil. Other tests have shown that an uncontaminated layer of soil increases the efficiency of the process to greater than 99.99%. Additional removal can be obtained by the use of charcoal filters in the off-gas treatment system, thus improving the overall system DRE to greater than 99.99%.

An engineering-scale test was conducted to evaluate the potential for destruction of a variety of containerized hazardous chemicals of specific interest were ethylene glycol, methyethyl ketone and stoddard solvent and photographic chemicals. The results indicate that an overall system DRE of >99.99% was achieved for each of the chemicals with no significant migration.

The observed system DREs indicate that the process has a potential to be a valuable tool for the remediation of sites that contain both organic and metallic hazardous wastes. However, we strongly recommend feasibility testing to confirm applicability before any commitment is given to deploy the process on a site that contains significant quantities of organics that are unconfined in the soil column.

APPLICATIONS CONSIDERATIONS

Before exploring various hazardous waste application scenarios, the operational capabilities and limitations of the large-scale system will be reviewed. The capabilities of the large-scale system to treat various soil characteristics and inclusions can be divided into two catagories: 1) capabilities of the power supply system and 2) the capacity of the off-gas system to maintain a negative pressure during processing. The capabilities of the electrical system in terms of electrode width, depth, and shape have been reported in Oma et al. (1983), Buelt and Carter (1986a), and Buelt et al. 1986.

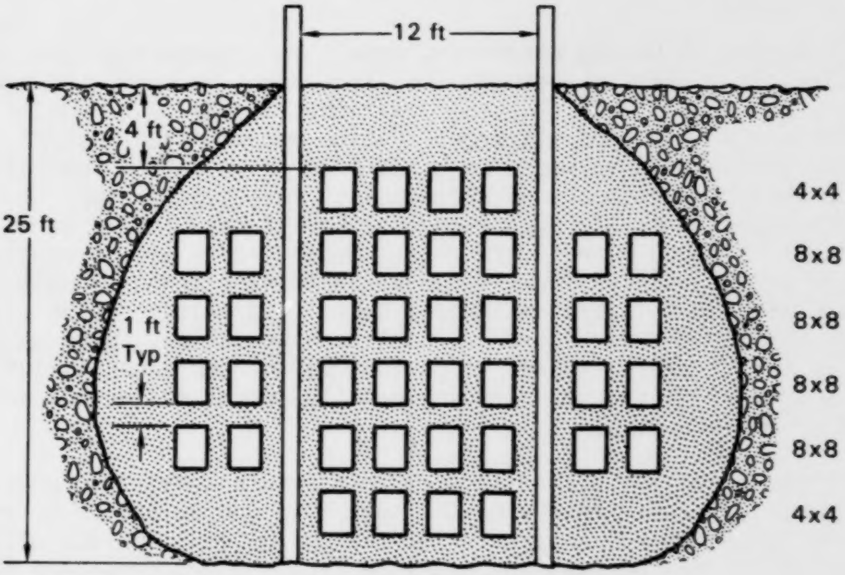
The two factors that can influence the ability of the power supply system are the presence of groundwater and buried metals. As a general rule, soils having low permeabilities do not inhibit the ISV process even in the water table because the rate of recharge is not significant in terms of the processing rate. The melt proceeds at a rate of about 3 to 6 in./hr. Thus, soils with permeabilities in the range of 10^{-5} to 10^{-9} cm/sec are considered able to be vitrified even in the presence of groundwater or in the water table. Soils with permeabilities in the range of 10^{-6} to 10^{-4} cm/sec are considered marginal. Soils with permeabilities higher than 10^{-4} are difficult to vitrify in the water table unless additional steps are taken, such as drawing the local water table down by pumping, and installing underground barriers. This is not considered a significant impediment because it is highly unlikely that any single method would be used to completely remediate a site. For example, ISV might be used to destroy/immobilize the source and standard pump and treat methods used to cleanup plumes that have migrated from the source.

The presence of buried metals can result in a conduction path that would lead to electrical shorting between the electrodes; however, the processing margins are quite generous. Buried metals that occupy up to 90% of the linear distance between the electrodes can be accommodated without suppressing the voltage between the electrodes or impacting the melting rate. Also, once melted, the impact of the metal is less significant. Miscellaneous buried metal, such as drums, should have little or no effect on the ability to process a candidate site. Metal limits are currently 5 wt% of the melt, which is a large fraction when considering drums of waste. In fact, drums containing hazardous and/or classified wastes can be placed in an array that will take advantage of the melt configuration. Such an array is shown in Figure 5. Here, the metal content of the 288 drums is 1.5 wt% of the melt weight, leaving considerable capacity for miscellaneous metal contained within the drums.

The capacity of the off-gas system to maintain a negative pressure during processing, thus preventing the spread of contamination or resulting in fugitive emissions, is a function of the gas generation rate within the processing area. Gas generation resulting from the decomposition of humus and other natural chemicals within the soil are considered insignificant. Gas generating situations are generically shown in Figure 6. These represent the intrusions of the molten glass into void spaces, penetration of a drum that contains combustible materials, and intrusion into soil inclusions that contain combustible materials, either solids or liquids. Schematically, the capacity of the off-gas system to contain the gas resulting from the processing event is shown in Figure 7. These capacities are representative of what might be encountered in a solid-waste burial ground. The capacities indicated for the liquid and solid combustibles disposed directly to the soil columns are considered as steady state processing limits. These limits do contain a safety factor of two, but should be considered as the processing limits at the present time. The release of the gas from either the void volume or combustible package is a transient event, lasting about 1 min. Therefore, once the transient event has passed, the system still has the capacity to handle another transient event. These are time-order limits, not cumulative capacities. The ISV process is particularly well suited to in-place destruction, immobilization or removal of hazardous waste. The toxic heavy metals are incorporated into the glass, and the organics in the containers are destroyed. Certain inorganic compounds such as nitrates are also destroyed by reducing the compound to the diatomic gases by the temperature and reducing conditions of the melt. Sulfates are partially decomposed; the remainder can easily be removed by the off-gas treatment system. Fluorides are dissolved into the glass to 98% for source terms of several hundred ppm. Chlorides are dissolved to the limits of solubility. These limits are much less than the limits for fluorides, but up to 1 wt% of the melt, which can be a large quantity. The fluorides and chlorides not dissolved in the glass can be scrubbed out by the off-gas treatment system, using a caustic scrub solution.

There are five general areas where the ISV process might be applied to hazardous waste: 1) contaminated soil sites, 2) burial grounds, 3) tanks that contain a hazardous heel in the form of either a sludge or salt cake, 4) classified waste that also contains hazardous waste, and 5) process sludges

Acceptable Conditions: 90% Linear Distance and 5 wt%



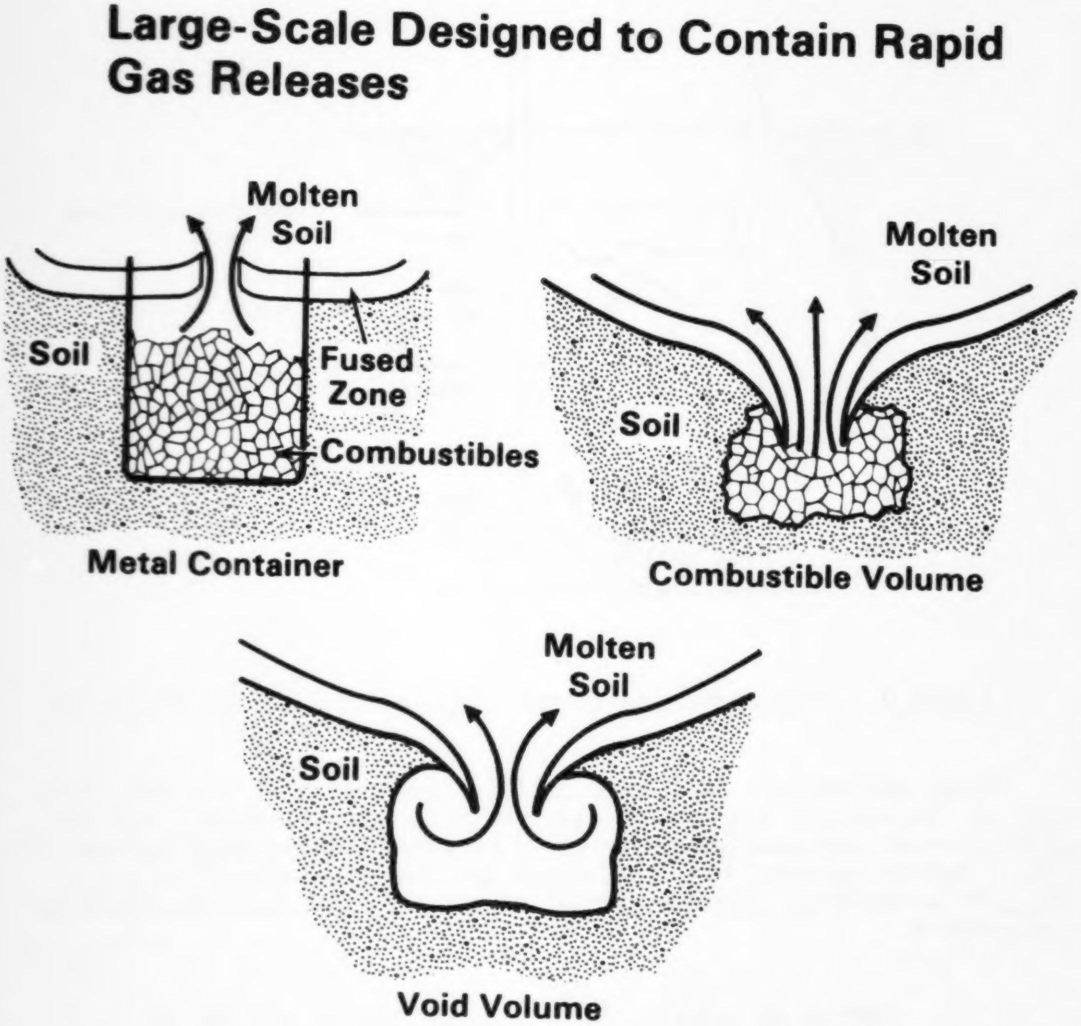
Metal wt = 1.5% of Melt Mass

FIGURE 5. Use of In Situ Vitrification for Buried Metals

and tailings piles. The application of the ISV process to contaminated soil sites and burial grounds is similar to the previously discussed applications to contaminated soils and burial ground sites, with the same processing limits for metal and combustibles.

The use of ISV to destroy the hazardous heel in tanks has been tested on the engineering scale with chemical salts. The results of the feasibility study showed that the release was within acceptable limits for the off-gas system and that a vitreous mass was formed. The original tests were performed on the basis of adding glass formers during the processing to achieve a vitreous waste form. The data could be extended to a scenario to dispose of the residual heel and the tank, and to immobilize contaminated soil in the immediate vicinity of the tank. By adding soil and/or rock backfill, the tank could be filled with glass-forming materials before processing. This technique could eliminate the concerns of tank dome and/or wall collapse identified during the original testing. Techniques for filling to the peak of the tank dome have been developed. Electrodes would be inserted into the tank prior to adding backfill. The vitreous area would grow downward and outward, encompassing the tank, the contents, and a portion of the surrounding soil. Estimates of the maximum size tank have not been completed, but tanks in the range of 100,000 to 300,000 gal could be permanently disposed by this technique. The metal content of the tank structure should not impose a processing limit.

Process sludges and tailing piles that contain natural radioactive materials and hazardous chemicals can be disposed using the ISV process. Applications that involve natural radioactive elements that result in relatively high radon fluxes at the surface are considered potential



Large-Scale Designed to Contain Rapid Gas Releases

Metal Container

Combustible Volume

Void Volume

FIGURE 6. Gas-Generating Configurations

candidates for remediation by ISV. Tests with zirconia-lime sludges showed that the material was not only able to be vitrified, but that the radon emanation level was reduced by a factor of 10^4 to 10^5 after processing. This solution is practical when the radon emanation levels are high, the wastes also contain hazardous chemicals that could be leached into the groundwater, and the local infiltration rate is high. In contrast, for large piles in remote areas and where the infiltration rate is very low, barriers over the pile have been shown to be effective in preventing release of hazardous chemicals. Each potential application must be examined on its own merit.

Valuable land that is contaminated can be reclaimed by using ISV processing, thus converting a corporate liability into a capital asset. Old transformer areas and capacitor storage and repair areas that are now in the business district, but contaminated with PCBs, are examples of this concept.

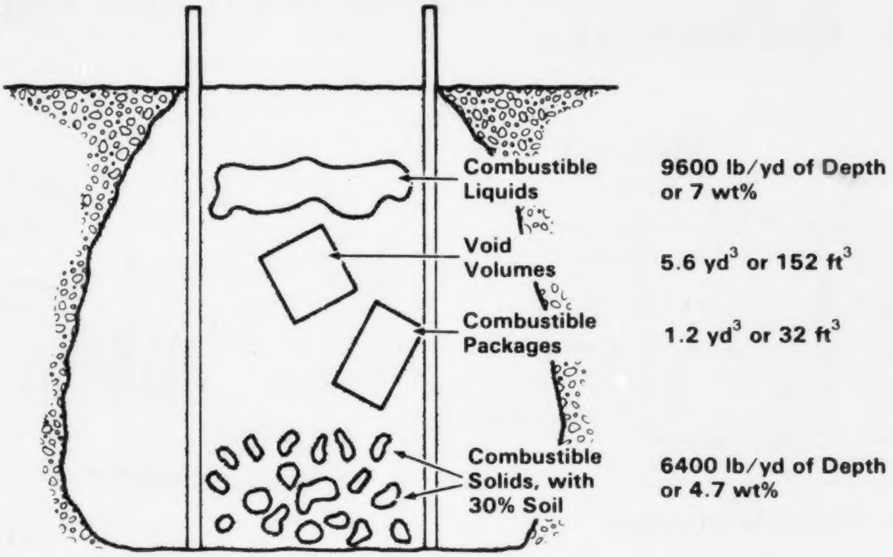

Combustible Liquids
9600 lb/yd of Depth or 7 wt%
Void Volumes
5.6 yd³ or 152 ft³
Combustible Packages
1.2 yd³ or 32 ft³
Combustible Solids, with 30% Soil
6400 lb/yd of Depth or 4.7 wt%

FIGURE 7. Combustible Limits for In Situ Vitrification Processing

Other applications considered, but not yet developed, include shaft sealing, foundations and erosion barriers for remote locations, and the generation of impermeable barrier walls to prevent groundwater seepage into a site. Barrier generation is considered an interim solution that would mitigate an existing hazardous situation until a final solution could be implemented.

SUMMARY OF PROCESS STATUS AND BENEFITS OF APPLICATION

The ISV process has been demonstrated at field-scale conditions, thus eliminating uncertainties of scale-up. This fact is significant because scale-up is the major risk area in the development and deployment of a new technology. Technology adaptation is a much smaller investment risk than technology development. The applicability of the ISV process to a particular waste can be determined with existing ISV equipment for a few thousand dollars. Thus, feasibility testing is relatively inexpensive. The focus of the feasibility testing is the performance requirements for the off-gas treatment system and the type and quantity of secondary waste generated. Because we know that almost all soils encountered can be vitrified, this is not a major consideration during most feasibility testing.

To date, experience indicates that the process is ready for deployment for soil sites contaminated with heavy metals and inorganics. Experience with low boiling point organics that are uncontaminated in the soil column is very limited, and feasibility testing with actual site samples before application is strongly recommended. The experience with PCBs, process sludges, and plating wastes is very encouraging. Although no single treatment process is applicable to all waste management needs, we anticipate that the ISV process will be used for a broader application of waste management problems. Within this context, ISV is a new and powerful tool that should be considered and evaluated for radioactive, mixed hazardous, and hazardous chemical applications that fall within the treatment capabilities of the process.

Specific benefits inherent in the ISV process are

- safety for workers and public
- long-term durability of the waste form (>1 million years)
- applicability to a variety of soils
- cost effectiveness ($100 to $250/ton for soils)
- volume reduction and immobilization for process sludges (<$100/ton)
- efficient processing rates (3 to 5 ton/hr).
- Reduced long term liability be avoiding land fill disposal.

The applicability of the ISV process to a wide variety of soils and wastes combined with its cost effectiveness, are responsive to the regulatory changes that are currently in progress, which emphasize the need for on-site and in situ permanent treatment and remediation.

ACKNOWLEDGMENT

The Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

REFERENCES

Buelt, J. L., and J. G. Carter. 1986a. In Situ Vitrification Large-Scale Operational Acceptance Test Analysis. PNL-5828, Pacific Northwest Laboratory, Richland, Washington.

Buelt, J. L., and J. G. Carter. 1986b. Description and Capabilities of the Large-Scale In Situ Vitrification Process. PNL-5738, Pacific Northwest Laboratory, Richland, Washington.

Buelt, J. L., et al. 1986. In Situ Vitrification of Transuranic Wastes: An Updated Systems Evaluation and Applications Assessment. PNL-4800, Suppl. 1, Pacific Northwest Laboratory, Richland, Washington.

Ewing, R. C., and R. F. Hocker. 1979. Naturally Occurring Glasses: Analogues for Radioactive Waste Forms. PNL-2776, Pacific Northwest Laboratory, Richland, Washington.

FitzPatrick, V. F., et al. 1984. "In Situ Vitrification - A Potential Remedial Action Technique for Hazardous Waste." PNL-SA-12316, Pacific Northwest Laboratory, Richland, Washington.

Larsen, T. and W. A. Langford. 1978. "Hydration of Obsidian." Nature. 276(9):153-156.

Oma, K. H., et al. 1983. In Situ Vitrification of Transuranic Wastes: Systems Evaluation and Applications Assessment. PNL-4800, Pacific Northwest Laboratory, Richland, Washington.

Timmerman, C. L. and K. H. Oma. 1984. An In Situ Vitrification Pilot-Scale Radioactive Test. PNL-5240, Pacific Northwest Laboratory, Richland, Washington.

Disclaimer

The work in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

CHARACTERIZATION AND TREATMENT OF WASTES COMPRISED OF HAZARDOUS, RADIOACTIVE MIXED, AND TRANSURANIC FRACTIONS

James T. Nelson
NUS Corporation
Oak Ridge, TN 37830

Richard A. Martineit
NUS Corporation
Gaithersburg, MD 20878

R. E. Helms
Martin Marietta Energy Systems, Inc.
Oak Ridge, TN 37831

ABSTRACT

This study addresses the characterization and treatment of a stratified radioactive wastewater stored in large underground tanks. The waste was tested in light of: USEPA's RCRA guidelines for hazardous wastes; and the Department of Energy's (DOE's) guidelines for radioactive mixed waste (RMW), low-level waste (LLW), and transuranic (TRU) waste.

Following these determinations, a regulatory analysis was performed to define the management guidelines for the various waste types. This analysis involved: USEPA/state hazardous-waste and wastewater regulations; applicable DOE Orders; and various guidelines promulgated by both DOE and the Nuclear Regulatory Commission (NRC).

Finally, the study addressed the treatment, storage, and disposal of the various waste types. Although further testing is necessary due to the unusual nature of the waste, preliminary conclusions have been made as to the most suitable treatment methods. The processes which appear to be the most acceptable, both from a technical and an economic standpoint, are: simultaneous volume reduction and solidification (VRS) using: asphaltic (i.e., bitumen) for the RMW and LLW fractions; and either asphaltic VRS or vitrification in soda-lime glass for the TRU fraction.

INTRODUCTION

Oak Ridge National Laboratory (ORNL), a major government-owned research facility, generates approximately 2000 gallons/month of wastewater from a wide variety of research and development activities. These streams are treated via ion exchange and/or evaporation; the resulting "clean" streams (i.e., evaporator overheads and effluent from ion-exchange beds) are discharged to surface waters through an NPDES outfall. The concentrated streams (i.e., evaporator bottoms and spent ion-exchange regenerant) are stored in eight 50,000-gallon underground storage tanks known as the Melton Valley Storage Tanks (MVSTs). From 1966-1984, this waste was mixed with grout and deep-well injected on site in a process known as "hydrofracture" (1,2). ORNL terminated this practice in January 1984 due to DOE/EPA/state concern that the deep aquifer may have been contaminated by migration of radioactive constituents from the hardened grout. Since that time, the concentrated wastes have been allowed to accumulate in the MVSTs. As of February 1986, the waste inventory had increased to approximately 328,000 gallons (3).

PURPOSE

Faced with potential curtailment and/or shutdown of the wastewater-generating processes, ORNL decided to select and implement one or more alternative processes to solidify/fix, and store or dispose of, the subject wastes. The processes were to be evaluated in light of their technical and economic viability, their permitting requirements, and their ability to produce waste forms whose properties conform to all applicable regulations and guidelines.

APPROACH

Waste Categories

The MVSTs were suspected to contain some combination of the following waste types: RCRA hazardous waste (HW); radioactive mixed waste (RMW); low-level waste (LLW); and transuranic (TRU) waste. The initial phase of this study consisted of a search of both the literature and applicable regulations/guidelines to clarify, to the extent possible, the definitions of these waste types.

Waste Characterization

Existing ORNL data (i.e., physical, chemical, and radiological parameters) were then evaluated in light of the various waste definitions. This enabled the proper classification of the waste strata in the MVSTs.

Evaluation of Regulations and Guidelines

ORNL's ultimate goal was to specify, and bring on line: one or more processes to solidify the MVST waste; and facilities/procedures for the proper storage and/or disposal of the resulting waste forms. These goals require knowledge of, and adherence to, numerous sets of regulations and guidelines (both internally- and externally-imposed). These "rules of the game" were evaluated in light of the restraints which they would place on the ultimate waste-management processes, facilities, and procedures.

Engineering and Economic Evaluation

Finally, existing solidification and storage concepts were studied to determine which would best meet ORNL's needs, both from the standpoint of engineering soundness and economic viability.

PROBLEMS ENCOUNTERED

Numerous problems were encountered in successfully performing this study. These were:

1) The regulatory definitions of two of the waste types (i.e., RMW and TRU waste) were vague. Accordingly, the authors used "hybrid" definitions based on current trends and perceptions.

2) When waste characteristics indicated the classification of a given sample as more than one waste type, it was not always clear which guidelines were to be followed. For example, wastes meeting the definitions of both HW and TRU waste were ultimately regarded as TRU.

3) Due to the nature of the wastes (i.e., high salt content and high

levels of radioactivity), analytical data lacked both the thoroughness and sensitive detection limits needed for a rigorous characterization effort. As a result, certain far-reaching, conservative assumptions had to be made. For example, uncertainties resulting from the inability to perform RCRA Extraction Procedure (EP) testing for heavy metals led to the conclusion that sludge samples were HW for the subject metals.

4) Most of the applications of the candidate solidification processes have been on LLW only, and not on TRU waste. Hence, it cannot be stated with certainty that the subject processes will produce waste forms which will meet the waste acceptance criteria (WAC) for TRU waste. However, due to the similarities between the WAC and 10 CFR 61, and the low heat generation rate of the Melton Valley wastes, it was assumed that the WAC would be met.

RESULTS

Waste Categories

The results of the waste-definition effort are as follows:

- RCRA Hazardous Waste (HW): The Resource Conservation and Recovery Act of 1976 (RCRA) spawned regulations dealing with (among other things) the identification and listing of HW. These regulations are located at 40 CFR 261.

- Radioactive Mixed Waste (RMW): The definition of RMW is not as clear as that for HW, and is still evolving among several agencies and their regulatory programs (4). DOE's current definition is: "... waste ... that would be subject to RCRA for the non-radioactive hazardous waste components and subject to (the Atomic Energy Act, or AEA) for the radioactive components." (5). A 1984 court decision (6) prompted DOE to bring RMW under the RCRA "umbrella" via an existing order (7).

- Low-Level Waste (LLW): LLW is defined in regulations promulgated by the Nuclear Regulatory Commission (NRC) as follows: "... radioactive waste not classified as high-level radioactive waste, transuranic waste, spent nuclear fuel, or byproduct material as defined in section 11e. (2) of the Atomic Energy Act ..." (10 CFR 61.2).

- Transuranic (TRU) Waste: The regulatory analysis revealed several different (although basically similar) definitions of TRU waste (7,8,9,10,11). For purposes of this study, the following "hybrid" definition has been selected: "TRU waste is waste which contains alpha-emitting radionuclides of atomic number greater than 92, half-lives greater than 20 years, and activity greater than or equal to 100 nCi/g."

Waste Characterization

In general, the waste stored in the MVSTs is a high-pH $NaNO_3$ solution. Although extensive characterization has been performed on the waste, the present study focuses only on those parameters which have to do with the waste types defined previously.

Initially, data were evaluated to determine whether or not the waste was RCRA hazardous. Since the subject stream is a mixture of aqueous wastes from numerous processes, it was judged not to be hazardous per 40 CFR 261.33 (e) and (f) (i.e., "P" and "U" wastes, respectively). Knowledge of the various waste-generating processes led to the conclusion that the waste did not contain hazardous waste from either nonspecific sources (40 CFR 261.31, or "F" waste) or specific sources (40 CFR 261.32, or "K" waste). This narrowed the search to the characteristics defined in 40 CFR 261.22: ignitable, corrosive, reactive, and toxic.

Due to high levels of both dissolved solids and radioactivity, extraction procedure (EP) metals analyses* were not performed. Moreover, ORNL's analyses of total levels of the metals were limited to: semi-quantitative spark source mass spectrometry (SSMS) on undiluted samples; and inductively coupled plasma (ICP) spectrometry on highly-diluted samples. Neither of these methods provides detection limits low enough to draw firm conclusions as to whether the MVST waste is characteristically toxic. The most that can be said is that the sludges in certain tanks are suspected to be EP toxic for barium, chromium, and lead (see Table 1).

Additional data reduction was performed to predict EP levels based on measured total levels; a discussion of these efforts, however, is outside the scope of this study. ORNL plans to upgrade its procedures and equipment to address the problem of high detection limits in radioactive samples. The literature provides guidance as to how private laboratories are dealing with this situation (12,13).

In light of the many uncertainties surrounding the EP toxicity issue, it was conservatively concluded that all of the MVST sludges are RCRA hazardous due to levels of one or more of the EP metals. Moreover, due to their levels of radioactivity, the sludges fall under the definition of RMW.

Regarding the MVST liquids, a RCRA determination was finally made on the basis of corrosivity. As stated in 40 CFR 261.22(a)(1), an aqueous waste is characteristically corrosive if its pH is outside of the range 2.0-12.5. Although pH was not measured directly, hydroxide normality was determined using a non-standard wet chemical/electrometric titration method (14); data are provided in Table 1. Since pH 12.5 corresponds to a hydroxyide normality of 0.032, it can be readily seen that samples of liquid layers from Tanks W-24, W-25, W-27, W-28, W-29, and W-30 exhibit pH values well above 12.5. Of the remaining tanks: no liquid sample was taken from W-31; and liquid samples from W-26 exhibit pH values of approximately 12. It was therefore conservatively concluded that all of the aqueous waste in the MVSTs is RCRA hazardous due to corrosivity. Moreover, due to its radioactivity, the liquid waste falls under the definition of RMW.

The remaining characterization issue consisted of a "TRU/non-TRU" determination. Table 1 shows activities, in nCi/g, of the TRU isotopes in various layers of the MVSTs. It can readily be seen that:

1) All of the "Top" and "Middle" samples tested well below the TRU minimum of 100 nCi/g.

---

* See 40 CFR 261.24 and Appendix II for a description of the EP characteristic.

Table 1. Chemical and radiological data on samples from the MVSTs

Tank	Location (1)	Hydroxide normality	pH (2)	Metals (mg/l)(3)			Sum of TRU isotopes (nCi/g)
				Ba	Cr	Pb	
W-24	Top	1.15	>14.00	70	5	<10	5.0
	Middle	1.18	>14.00	40	5	10	10.3
	Bottom	1.23	>14.00	6000	50	200	142
	Sludge	--	--	100	100	100	679
	Liquid	0.92	13.96	--	--	--	--
	Solids	--	--	--	--	--	630
W-25	Top	0.67	13.83	30	10	10	16.8
	Middle	0.65	13.81	30	10	<10	16.3
	Bottom	1.00	14.00	50	50	50	126
	Sludge	--	--	50	50	100	347
	Liquid	0.61	13.79	--	--	--	--
	Solids	--	--	--	--	--	800
W-26	Top	0.01	12.00	200	10	5	15.9
	Middle	0.01	12.00	100	10	<5	17.7
	Bottom	<0.01	<12.00	20	20	10	24.3
	Sludge	--	--	70	100	10	137
	Liquid	0.01	12.00	--	--	--	--
	Solids	--	--	--	--	--	630
W-27	Top	0.24	13.38	200	20	<10	15.6
	Middle	0.25	13.40	100	20	<10	17.5
	Bottom	0.26	13.41	100	40	10	46.7
	Sludge	--	--	100	30	20	50.7
	Liquid	<0.01	<12.00	--	--	--	--
	Solids	--	--	--	--	--	510
W-28	Top	0.02	12.30	3	3	<3	0.7
	Middle	0.02	12.30	10	3	<3	0.6
	Bottom	0.40	13.60	30	20	<10	59.7
	Sludge	--	--	20	20	50	77.8
	Liquid	0.04	12.60	--	--	--	--
	Solids	--	--	--	--	--	210
W-29	Liquid	0.80	13.90	--	--	--	--
	Solids	--	--	--	--	--	1080
W-30	Liquid	1.00	14.00	--	--	--	--
	Solids	--	--	--	--	--	260
W-31	Solids	--	--	--	--	--	770

Notes:

1) Descriptions of sampling campaigns and locations are provided in Peretz, pp. 10-14.
2) pH values were calculated from the measured values of hydroxide normality.
3) As measured by spark source mass spectrometry (SSMS).

2) "Bottom" samples in Tanks W-26, W-27, and W-28 tested less than 100 nCi/g.

3) "Bottom" samples in Tanks W-24 and W-25 tested greater than 100 nCi/g.

4) "Solids" samples in all tanks tested significantly greater than 100 nCi/g (average level was 661 nCi/g).

5) "Sludge" samples showed an average level of 258 nCi/g. The differences between "Sludge" and "Solids" results are believed to be due to the more vigorous agitation of the tanks prior to withdrawal of the "Sludge" samples. This action caused the more-radioactive settleable solids to be more widely dispersed throughout the tank contents, with a resulting dilution in the concentrations of TRU isotopes in the tank bottoms.

As a result of these measurements, it was concluded that the "Solid" waste fraction (as defined in Peretz, p. 12), plus any filterable solids from the aqueous fractions, were to be regarded as TRU waste. The conclusion that TRU waste is almost exclusively in the solid phase is further supported by centrifugation/filtration studies performed at ORNL (15).

Regulatory and Engineering Evaluation

Figure 1 provides a simplified process flow diagram (PFD) of the waste management scheme proposed to ORNL. The diagram is keyed to the following descriptions of waste streams, processes, and applicable regulations and guidelines:

1) Liquid MVST waste is RMW (due to pH 12.5 and measurable radioactivity).

2) Both MVST sludge and filtered solids are TRU waste (due to the presence of alpha-emitting radionuclides of atomic number greater than 92, half-lives greater than 20 years, and activity greater than 100 nCi/g).

3) In consideration of both technical and regulatory constraints, wastes will be "campaigned" through the solidification facility. Asphaltic solidification is planned for both the RMW and TRU waste fractions. However, if the TRU waste form fails to meet specifications (see #7 below), soda-lime vitrification may have to be employed. The latter option would be considerably more expensive than asphalt. Whichever process is used, the solidification facility will not be subject to RCRA permitting due to the "wastewater treatment unit" exemption in Tennessee Rule 1200-1-11-.01(2)(a).

4) Condensed liquids resulting from the VRS process will be discharged via an existing NPDES-permitted outfall.

5) The asphalt waste form resulting from RMW treatment must meet federal regulations for LLW (10 CFR 61.56). It will not be a RCRA waste, since the leachability will preclude classification as EP toxic. However, delisting - per 40 CFR 260.22 - may have to be pursued.

6) The engineered storage facility will not be regulated under RCRA, since neither waste form will be a hazardous waste. However, the facility will have to meet the

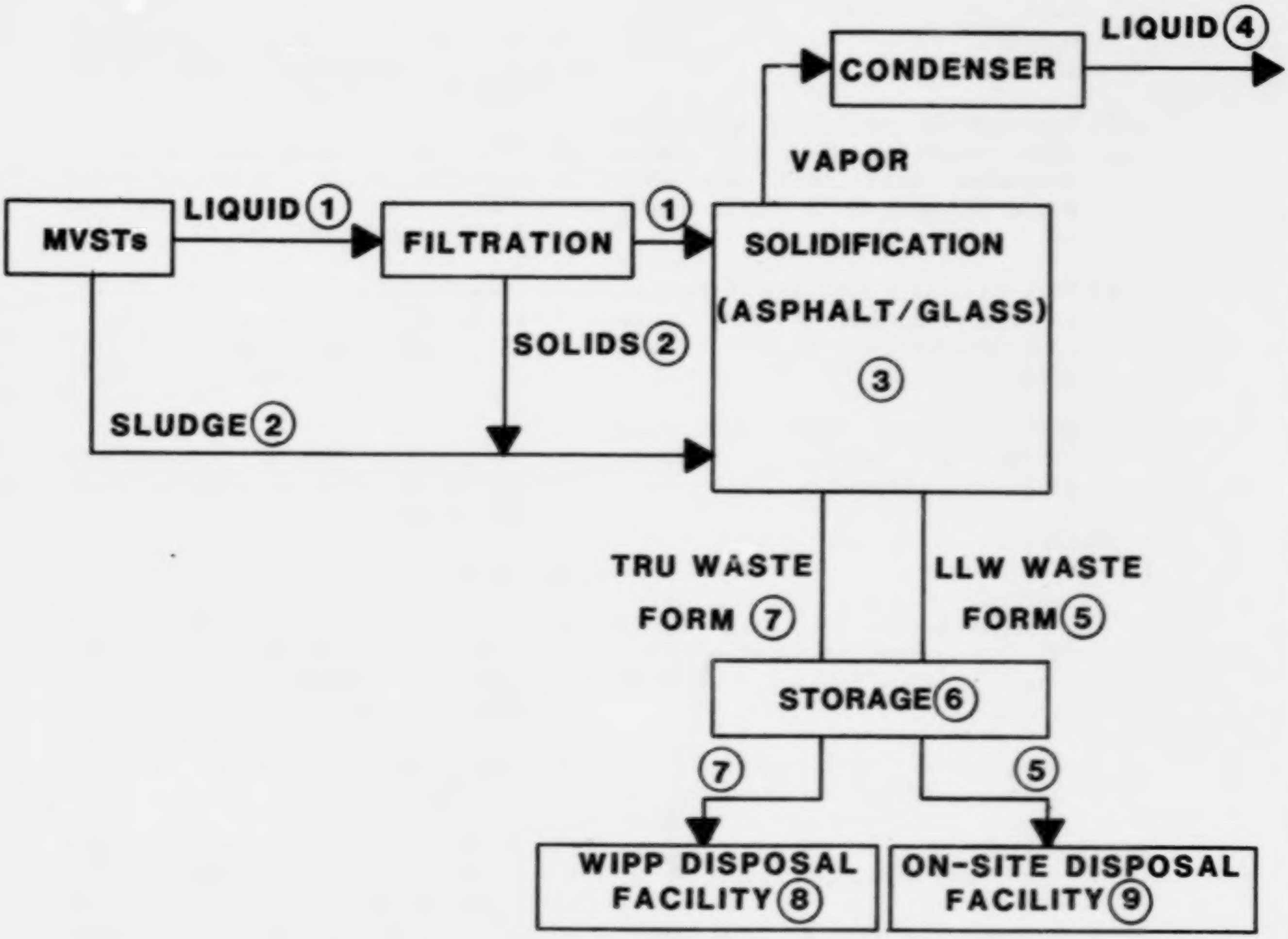

LIQUID ④
CONDENSER
VAPOR
MVSTs
LIQUID ①
FILTRATION
①
SOLIDIFICATION
(ASPHALT/GLASS)
③
SOLIDS ②
SLUDGE ②
TRU WASTE
FORM ⑦
LLW WASTE
FORM ⑤
STORAGE ⑥
⑦
⑤
WIPP DISPOSAL
FACILITY ⑧
ON-SITE DISPOSAL
FACILITY ⑨

FIGURE 1 - Process Flow Diagram of Proposed Waste Solidification, Storage, and Disposal Processes at ORNL

design criteria given in: "Design Guidance for Temporary Onsite Storage of Low-Level Radioactive Waste", NUREG-0800, Appendix 11.4-A; and DOE Order 5820.2.

7) The asphalt (or vitrified) waste form resulting from TRU waste treatment must meet the WIPP Waste Acceptance Criteria (WAC) (8).

8) This is a DOE facility dedicated to the disposal of TRU waste from defense-related DOE activities.

9) This facility must meet the design and operating criteria given in 10 CFR 61.

REFERENCES

1. Weeren, H. O., et al, 1974. "Hydrofracture Site Proof Study at Oak Ridge National Laboratory", ORNL-TM-4713, November 1974.
2. Stow, S. H., and Haase, C. S., 1986. "Subsurface Disposal of Liquid Low-Level Radioactive Wastes at Oak Ridge, Tennessee", CONF-860307-1, 1986.
3. Peretz, F. J., et al, 1986. "Characterization of Low-Level Liquid Wastes at the Oak Ridge National Laboratory", ORNL/TM-10218, December 1986, p. 6.
4. "Primer on Mixed Radioactive and Hazardous Wastes", The Hazardous Waste Consultant, September/October 1986, pp. 4-1 through 4-22.
5. Farber, K., "Presentation to the Defense Program's Techical Review Group Regarding Hazardous and Mixed Waste Activities of the Department of Energy", July 23, 1986 (unpublished).
6. Legal Environmental Assistance Foundation v. Hodel, Civ. 3-83-562, April 13, 1984.
7. Hazardous and Radioactive Mixed Waste Management, DOE Order 5480.2, 12/13/82.
8. "TRU Waste Acceptance Criteria for the Waste Isolation Pilot Plant", WIPP-DOE-069, Revision 2, September 1985, p. 13.
9. "Feasibility Study for RH-TRU Waste Handling Facility", X-OE-254, Martin Marietta Energy Systems, Inc., September 28, 1984, Table B.1.
10. Radioactive Waste Management, DOE Order 5820.2, 2/6/84, Section 6.aa.
11. Peretz, op. cit., p. 60.
12. Leventhal, L., "Analytical Experience with Mixed RCRA and Low Level Waste", presented at HazMat 85 West, Hazardous Materials Conference and Exhibition, Long Beach, California, December 3, 1985.
13. Kharkar, D. P., et al, "The Laboratory Protocol for Co-Contaminated Waste", Proceedings of the Nineteenth Mid-Year Topical Symposium of the Health Physics Society, Knoxville, Tennessee, February 2-6, 1986.
14. Ibid., p. 32.
15. Ibid., p. 61.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

A METHOD FOR PREDICTING QUALITY IN SOLIDIFIED HAZARDOUS WASTES

Dent C G, Rushbrook P E, Baldwin G
Waste Research Unit Harwell Laboratory
Oxfordshire, OX11 0RA
United Kingdom

ABSTRACT

The solidification process is one option for treatment of hazardous wastes prior to disposal. Unfortunately, information on the physical and leaching characteristics of a waste mix do not become available until many days after preparation. In this paper, a novel concept is proposed for predicting the final quality of a solidified waste at the time the mix is prepared. The procedure should aid both operators and regulators of the solidification process. The proposal follows the results of a programme of research funded by the UK Department of the Environment and conducted by the Waste Research Unit at Harwell into the cement-based solidification technique. Trial mixes of different compositions of both liquid and solid waste, cement and PFA were made up and subsequently tested for rate of setting, hydraulic conductivity, compressive strength, supernatant production and leaching characteristics. The results were combined with arbitrary regulatory criteria to produce conceptual quality control charts.

INTRODUCTION

The number of routes available for the disposal of hazardous wastes is limited. Landfill is in many cases not a disposal option unless the waste has undergone some form of pretreatment. One such treatment process is solidification. In general terms, the process involves mixing the waste with chemical additives such that the hazardous components of the waste become immobilised in the solid matrix which develops. Various solidification techniques are described in the literature (10,14) and the process has been patented for a wide range of inorganic wastes (9,16-20). Some examples include:

i) Cement-based techniques;
ii) Silicate-based techniques;
iii) Pozzolanic processes (not containing cement);
iv) Thermoplastic techniques including the incorporation of bitumen, paraffin and polyethylene;
v) Organic polymer techniques (including urea-formaldehyde and unsaturated polyester);
vi) Surface encapsulation (jacketing);
vii) Vitrification processes.

A satisfactory process is one which not only limits the rate of leaching of hazardous components to environmentally acceptable levels, but also produces a product with adequate physical characteristics.

Within the UK, commercial application of solidification processes has been largely confined to the cement-based technique for treatment of inorganic wastes. It is apparent that a clear understanding of the chemical and physical processes occurring within mixes undergoing solidification by this technique is only just emerging (6-8,13,14,21). Briefly, it is considered that the mechanisms involved include attenuation by chemical absorption, formation of metal complexes and entrapment within the hydrated calcium silicate matrix which forms after mixing. The technique is particularly suitable for acid wastes (such as those from the metal finishing industries) since the cement provides both a capacity to neutralise the acid as well as a capacity to remove heavy metals. Application of the cement solidification technique for organic wastes has been relatively unsuccessful although some limited success has been reported (15). The literature also refers to the successful use of absorbents for organic wastes prior to solidification (14).

The paper discusses the objectives and results of a programme of research into the cement-based process, conducted by the Waste Research Unit at Harwell and funded by the UK Department of the Environment. Some of the results of the programme are given, together with an overview of a new concept for quality control of the solidification process.

PURPOSE

For solidification processes in general, there are a number of areas of legitimate concern. These include:

i) Laboratory tests. How representative are the results of these to the real field situation?

ii) Long-term stability. How will the product deteriorate over many years with leaching of calcium and exposure to extremes of temperature and other conditions?

iii) Quality Control. How can it be best ensured at the time of mixing that the mix will ultimately meet the necessary regulatory (say 28-day) physical and leaching criteria?

This paper addresses itself mainly to issues related to item (iii). Issues related to item (i) are also discussed briefly. With regard to (ii), this is an area of major uncertainty which only long-term monitoring may help to clarify.

In recent years, instances have been reported in which the quality of solidified waste has not met the standards expected by the regulatory authority (2,12). One of the purposes of this work was therefore to investigate in detail for a wide range of wastes the range of mix compositions which can be expected to produce both satisfactory and unsatisfactory solidified products.

A further major purpose was to look at the whole concept of quality control. One of the problems which currently faces any regulatory authority is its lack of control over this treatment process at the time the mix is prepared. For example, one of the criteria commonly used to indicate satisfactory performance is the rate of setting of the solidifying mix. In the standard BS procedure for penetrometry testing (4) which has been adapted for use in testing solidifying wastes, the 28-day measurement is approximated to 95% of final strength. Hence, as an example, one authority in the UK has set as a standard a cone penetration of less than 1.5mm after 28 days (and less than 3.5mm after 7 days). The information on the acceptability of the mix only becomes available after the mix has been deposited. The Waste Research Unit has therefore suggested the concept of "quality control charts" which are drawn up from the extensive pre-testing and can subsequently be used to assess the likely acceptability of a waste mix at its time of production.

APPROACH

Selection of PFA

Ordinary Portland Cement (3) was used in the preparation of all mixes and in most cases, pulverised fuel ash (PFA) was also incorporated as a bulking agent. However, PFA is not a consistent product; its composition and behaviour can vary markedly from one source to another. Some separate experiments were therefore conducted to investigate the reproducibility of cement setting rates when the cement was partially substituted by different PFAs. This reproducibility has important implications for the quality control procedure discussed later. Samples of three PFAs were mixed with cement and water in the ratios of 3:1:1 and setting rates were measured over 8 days using a cone penetrometer.

Preparation of Mixes

The wastes investigated within the laboratory programme were selected on the basis of their being representative of large arisings typically treated by the cement-based process within the UK. These include:

i) Liquid cyanide waste;
ii) Solid cyanide waste;
iii) Mixed inorganic acid waste;
iv) Caustic waste solution;
v) Metal-bearing slags.

The programme was divided into two stages. The first stage included the production of poorly prepared mixes subjected to a minimum of pretreatment i.e. representative of a poorly run operation. The results of this stage are not discussed in this paper. However, they did help to identify a "grey area" between compositions likely to give rise to acceptable and unacceptable products. In the second stage, pretreatment was much more rigorous and the preparation was intended to be more representative of a well run operation. Mix compositions were focussed around the "grey area".

Pretreatment of the wastes included size reduction of metal slags, oxidation of cyanide by treatment with sodium hydroxide and sodium hypochlorite (pH greater than 10.5) and neutralisation of both caustic and acid wastes to pH 7.0. The preparation of samples followed the sequence of events to be expected at a commercial plant i.e. pretreatment, mixing of wastes, addition of PFA, further mixing, addition of cement, and then final mixing. The compositions of the trial mixes for the second stage are given in Table 1.

Parameters measured

Parameters measured included the following:

i) rate of setting;
ii) rate of supernatant production;
iii) compressive strength after testing;
iv) hydraulic conductivity;
v) concentrations of heavy metals in the leachates.

Approximately 1.5 kg of each waste mix were produced. 750g of each were poured into trays measuring 17cm x 12cm x 6cm to a depth of 2.5cm. The trays were left to set in a cool room, away from draughts and disturbances. The tray samples were used to determine the rates of setting and supernatant production as well as providing later sub-samples for compressive strength and leaching tests. Further samples of 300-400g were placed into cylindrical moulds for hydraulic conductivity testing.

Brief details only are given here of the methods used for each test. The rate of setting was determined from penetration readings made with an 80g cone which conforms to the specifications in BS 1377:1975 (4). Supernatant depths were measured on a daily basis. Compressive strength tests were conducted after 28 days on cubes of material, approximately 25mm x 25mm x 25mm, cut from the solidified mixes within the trays. Testing was performed on a machine conforming to the British Standard for the compression testing of hardened cement paste and concrete (5). Each sample was stressed at the recommended rate of 15 MPa min

The general procedure followed for the hydraulic conductivity tests followed a standard method reported in the literature (1) but with a number of modifications. Measurements of hydraulic conductivity were made after 7 and 28 days. Leaching tests were performed on samples 28 days after preparation using the standard Waste Research Unit method (11). The leachates were filtered and analysed for cadmium, copper, iron, nickel, lead, zinc, (and arsenic on a more limited basis).

Testing of bulk samples

An extra 5 kg of mixes 11, 14 and 15 (Table 1) were prepared and poured into tanks measuring 20cm x 15cm x 15 cm. The purpose was to compare the setting rates of the mixes in these containers with those in the shallow deep trays and hence give an indication of any variation in behaviour to be expected in the landfill where the depth of layering may vary substantially. Setting rates were again determined from 80g cone penetration measurements.

PROBLEMS ENCOUNTERED

The major problem encountered was in obtaining reproducible results from the hydraulic conductivity tests. Two sets of apparatus were constructed. In the first apparatus, the waste was contained within a rigid aluminium container whose inside walls had been coated with fine sand to promote adhesion with the waste. A column of water above the sample was kept at a constant head. As the mixes solidified, they shrank and fissures developed between the sample and container wall. Preferential flowpaths developed which produced overestimates of hydraulic conductivities. With the second piece of apparatus, the rigid container was replaced by an elastic rubber membrane. Newly prepared mixes were poured into split moulds and left to set for 28 days after which time each 5cm core was removed from its mould and placed into the membrane. In this case, the added physical handling involved unfortunately disturbed some of the samples (i.e. they become less intact). Whilst this method overcame the previous problems, with lower hydraulic conductivities being recorded, reproducibility was still poor. Further work is now planned to establish a more reliable method of testing.

With the compressive strength testing, the need to conserve sufficient quantities of the samples for leaching tests demanded that the dimensions of each cube were less than those normally recommended in the BS standard (100mm x 100mm x 100mm). No correction factors were applied to the results.

RESULTS

Selection of PFA

The results indicated that one of the PFAs displayed a very different setting rate over 8 days to that of the others. The source and composition of PFA may therefore be an important factor in the solidification process. The PFA displaying the best setting rate was selected for the subsequent tests.

Sample Mixes

The scope of this paper does not allow a detailed description of the results. A brief summary is however given of the results for setting behaviour. Some of the results for the other tests are in effect summarised in Figure 2 (referred to later), in so far as the performances of the different mixes are assessed against a range of arbitrary criteria.

During the first 10 days, setting rates were high but declined rapidly thereafter. The most noticeable influence was the proportion of liquid waste in the mix. Five days after preparation, mixes with greater than 40% liquid waste generally achieved no more than 60% of their final strength (i.e. 28-day value). The mixes with less than 40% liquid waste set more rapidly, producing between 72% and 98% of final (28 day) strength. Figure 1 shows the results of the 7-day cone penetrometer measurements. From this figure, it can be seen that for those compositions including 4% cement, seven out of eight mixes produced samples with poor rates of setting (greater than 3.5mm). However, with an increase to 7% cement content, the performance improved noticeably with some previously poor mixes now recording depths of less than 1.5mm. The relationship between improvement in strength and increasing cement content was less firm for mixes with higher proportions of liquid waste.

A similar diagram was plotted for the 28-day results (and indeed for all other tests) but is not included here. Very similar trends were observed to those described above.

Comparison of Bulk and Standard Samples

The bulk samples generally solidified at a much slower rate than the standard samples, although after a period of 7 days the rates converged, with penetrometer measurements for bulk samples lying between 0.5-1.0mm and for standard samples between 0.1-0.2mm by Day 28. Nevertheless, applying acceptability criteria of less than 1.5mm at Day 7 and less than 0.5mm at Day 28, then bulk mixes 14 and 15 would have failed, whereas the standard samples would have passed. Under these circumstances, it clearly becomes very important that trials are carried out to establish the relationship between laboratory tests and likely field effects. This relationship would then have to be taken into consideration when regulatory criteria based on laboratory tests were set.

Quality Control Charts

Reference has already been made to one of the major difficulties facing both operators and regulators of solidification processes i.e inadequate control at the time of mixing. Although the procedure outlined here is still at a development stage (and certainly requires further refinement), it is nevertheless put forward as a concept which shows considerable promise in terms of providing a tool to both regulator and operator in assuring the quality of the final solidified products. The procedure would be site-specific and involve three stages.

In the first stage, a range of physical tests including perhaps setting rate, compressive strength, supernatant retention and hydraulic conductivity would be conducted on mixes made up from the bulk waste stream, cement and PFA. It is envisaged that 20 to 30 mixes would be prepared, representing a broad range of compositions. Results would be plotted onto triangular diagrams (e.g. Fig 1) and assessed against the relevant criteria set by the regulatory authority. The second stage would involve heavy metal leaching tests on those samples satisfying these criteria. These results would in turn be assessed against any water quality limits set on the leachates.

From inspection and assessment of the above diagrams, the third stage would then involve the preparation of a quality control chart such as that suggested in Figure 2. The chart would incorporate contours indicating the constraints on mix composition to meet the different regulatory criteria. Resulting from this, the chart would in effect identify a zone of mix compositions which, from the testing programme, would be expected to produce "acceptable" final products. Such a zone is shown in Figure 2.

It is suggested that the control chart could become a requirement of the operator's disposal site licence or permit. During inspection visits, the operator would be required to divulge details of the mix composition to the regulator. This could then be assessed against the "zone of acceptability" on the chart. To verify the operator's information on compositions, it might be possible to install security-locked flow meters or weighing equipment on input flow lines, or the mixer itself could be mounted on a weighing device. The regulatory authority might also on occasions wish to take its own samples of the bulk waste stream and mixes under preparation, and check its own results against those predicted by the chart.

The charts themselves would need to be reviewed from time to time, especially in the following situations:

i) when the composition of the bulk waste stream varied by more than a predetermined value, or the source or composition of cement or PFA likewise changed;
ii) significant modifications were made to the pretreatment or solidification process;
iii) if the regulatory limits were altered;
iv) at regular intervals (say 2-3 years) to ensure the chart was still reliable.

In order to refine the procedure outlined above, the Waste Research Unit is now planning to validate the results of its work to date. This will include a programme of tests undertaken in conjunction with a treatment plant operator in which laboratory results will be compared against those achieved in the field.

ACKNOWLEDGEMENTS

This work has been funded by the UK Department of the Environment (DoE). The authors wish to thank members of the DoE's Land Wastes Division for their advice and assistance.

REFERENCES

1. American Society of Agronomy. Methods of Soil Analysis. Ed. Black, C A. Part 1, pp 520-531.

2. Anon, Getting to Grips with Waste Solidification. ENDS Report 120, January 1985, pp 11-13.

3. British Standard (BS) 12 (1958); 4027 (1966), 4248 (1968), 146 (1968), 4246 (1968), 1370 (1958), 915 (1947). British Standards Institution.

4. British Standard (BS) 1377. (1975). British Standards Institution.

5. British Standard (BS) 4550: Part 3: Section 3.4 (1978). British Standards Institution.

6. Brown, T M, Bishop, P L. The Effect of Particle Size on the Leaching of Heavy Metals from Stabilised/Solidified Wastes. Proceedings of New Frontiers for Hazardous Waste Management International Conference, Pittsburgh, 15-18 September 1985, pp 356-363.

7. Clark, A I, Poon, C S, Perry, R. The Rational Use of Cement-Based Solidification Techniques for the Disposal of Hazardous Wastes. Proceedings of New Frontiers for Hazardous Waste Management, International Conference, Pittsburgh, 15-18 September 1985, pp 339-347.

8. Eaton, H C, Tittlebaum, M E and Cartledge, F K. Techniques for Microscopic Studies of Incineration and Treatment of Hazardous Waste, Eleventh Annual Research Symposium, Cincinnati, Ohio, 29 April-1 May 1985, pp 135-142.

9. European Patent, No 0013822 (1979).

10. Guide to the Disposal of Chemically Stabilized and Solidified Waste. United States Environmental Protection Agency. US Army Engineer Waterways Experiment Station, Mississipi, 1980, SW872.

11. Harwell Report. The Testing of Hazardous Wastes to Assess Their Suitability for Landfill Disposal. AERE R10737 (1982).

12. Hazardous Waste Management - An Overview. First Report of the UK Hazardous Waste Inspectorate, June 1985.

13. Poon, C S, Clark, A I, Perry, R. Permeability Study on the Cement-Based Solidification Process for the Disposal of Hazardous Wastes. Cement and Concrete Research, 1986, Vol 16, Pergammon Press Ltd, pp 161-172.

14. Reimann P. Solidification, A Hazardous Waste Treatment with Many Aspects. 3rd International Symposium on Operating European Hazardous Waste Management Facilities, Odense, Denmark, September 1986.

15. Tittlebaum M. Correlations between the Microstructure and Measured Physical Properties of Solidified Organic Hazardous Wastes. 3rd International Symposium on Operating European Hazardous Waste Management Facilities, Odense, Denmark, September 1986.

16. United Kingdom Patent, No 148525 (1973).

17. United Kingdom Patent, No 2016438A (1978).

18. United Kingdom Patent, No 2040712A (1979).

19. United States Patent, No 4230568 (1978).

20. United States Patent, No 4154307 (1985).

21. Walsh, M B, Eaton, H C, Tittlebaum, M E, Cartledge, F K and Chalasani D. The Effect of Two Organic Compounds on a Portland Cement-Based Stabilisation Matrix. In Hazardous Waste and Hazardous Materials, 1986, Vol 3, No 1, Mary Ann Liebart, Inc, Publishers, pp 111-123.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

TABLE 1
Composition of each sample waste mix

Stage of study	Sample number	Cement	Liquid waste				Solid waste		
			Oxidised solid cyanide waste (in liquid form after oxidation)	Oxidised liquid cyanide waste	Neutralised acid/alkali	Total liquid waste	PFA	Metal slags	Total solid waste
Stage 2	1	2	23	21	21	65	17	16	33
"	2	2	18	16	16	50	24	24	48
"	3	2	14	13	13	40	29	29	58
"	4	2	10	10	10	30	34	34	68
"	5	4	19	18	18	55	21	20	41
"	6	4	15	15	15	45	26	25	51
"	7	4	13	11	11	35	31	30	61
"	8	4	9	8	8	25	36	35	71
"	9	7	20	20	20	60	17	16	33
"	10	7	18	16	16	50	22	21	43
"	11	7	14	13	13	40	27	26	53
"	12	7	10	10	10	30	32	31	63
"	13	9	19	18	18	55	18	18	36
"	14	9	15	15	15	45	23	23	46
"	15	12	18	16	16	50	19	19	38
"	16	12	14	13	13	40	24	24	48
"	17	14	23	21	21	65	11	10	21
"	18	14	19	18	18	55	16	15	31
"	19	14	15	15	15	45	21	20	41
"	20	17	18	16	16	50	17	16	33

All percentages are rounded to the nearest whole number.

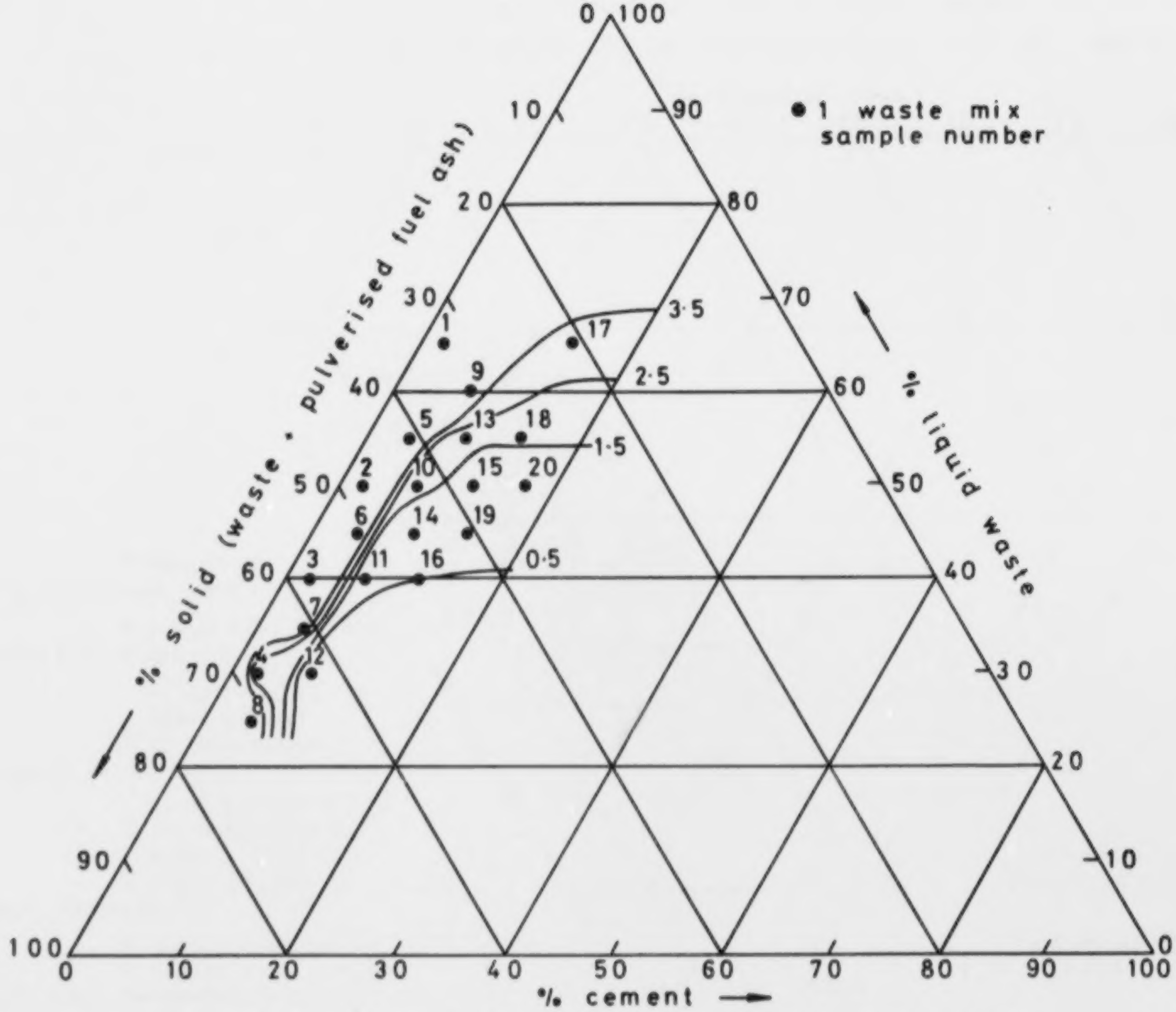


Figure 1 . Day 7 penetrometer measurements plotted against waste mix compositions (mm)

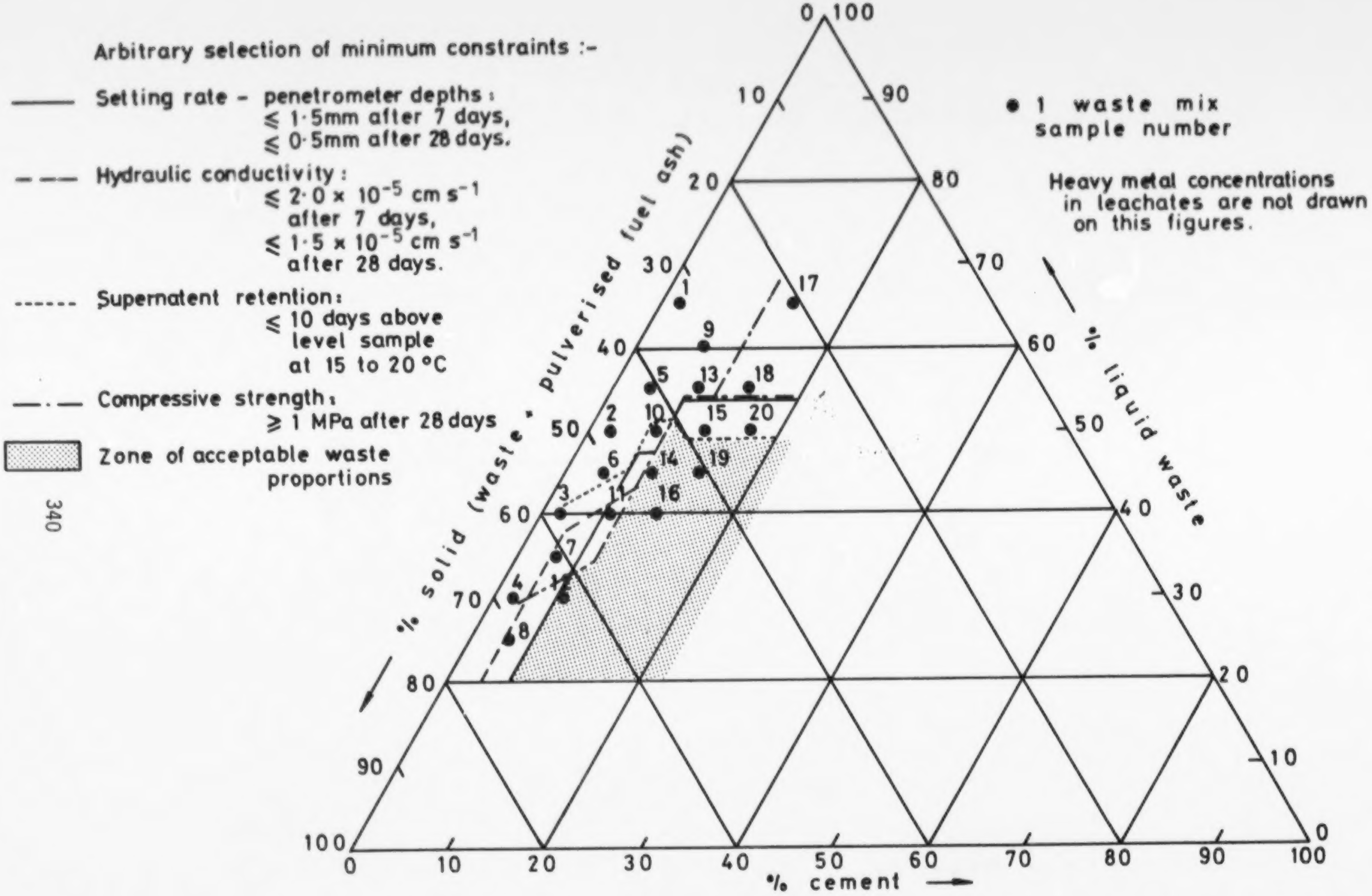


Figure 2. An example of a solidification control chart with a suggested "zone of acceptable waste proportions"

INTERLABORATORY AND INTRALABORATORY REPRODUCIBILITY OF RESULTS OF AN INVESTIGATION OF TEST METHODS FOR SOLIDIFIED WASTE CHARACTERIZATION

J. Stegemann
Environment Canada
Conservation and Protection
Wastewater Technology Centre
867 Lakeshore Rd., P.O. Box 5050
Burlington, Ontario, L7R 4A6

ABSTRACT

Solidification processes are designed to improve wastes for landfilling by ameliorating their physical properties, or immobilizing the contaminants to prevent groundwater contamination, or both.

The numerous vendors of solidification processes make various claims as to the degrees to which their processes affect the properties of concern. At present, no set of standard tests exists for measuring the efficacy of solidification processes.

A cooperative program was conducted to develop a protocol of laboratory test methods for determining the intrinsic physical and chemical characteristics of solidified wastes.

This protocol of test methods includes seven physical tests: Bulk Density, Solids Specific Gravity, Water Content, Unconfined Compressive Strength, Hydraulic Conductivity and Freeze/Thaw and Wet/Dry Weathering Resistance, and five chemical tests: Equilibrium Extraction, US EPA Toxicity Characteristic Leaching Procedure (TCLP), Acid Neutralization Capacity, Sequential Chemical Extraction and Dynamic Leach Test (1).

The objectives of the program were: 1) to investigate the suitability of the twelve test methods for characterizing a large variety of solidified wastes, and 2) to create a data base of the properties of solidified wastes which will assist in setting standards and provide a basis for further developmental work.

The participants in this study were Environment Canada, the US Environmental Protection Agency, Alberta Environment, and fifteen companies involved in developing or marketing solidification technology. Each of the fifteen industrial participants used the solidification process of their choice to treat as many as five wastes. Testing of the solidified products was carried out at Environment Canada's Wastewater Technology Centre (WTC), the Alberta Environmental Centre (AEC), and US Army Corps of Engineers' Waterways Experiment Station (WES).

In order for a test method to be suitable for measuring a property in a variety of solidified wastes, two criteria must be met: 1) it must be capable of measuring a range of values for a particular property, and 2) it must be practical and reproducible within and between laboratories.

The range of values measured for the different solidified products for each test and each waste type has been discussed elsewhere (2).

This paper will deal with the reproducibility of the test methods within and between laboratories. There are a number of potential sources of variability: heterogeneity of the raw waste, heterogeneity of the solidified waste, and variation of the test procedure or chemical analytical methods for different technicians in different laboratories.

Multiple samples of each of the raw wastes and each of the solidified products were analysed to determine homogeniety.

In general, quadruplets of each test were conducted, with duplicate testing of each sample in two laboratories. Interlaboratory reproducibility of each test method was determined by plotting the value measured in one lab vs the value measured in the other; intralaboratory reproducibility was determined by plotting the value measured for one replicate vs the value measured for the other. In both cases, reproducibility was judged to be good if the plotted points approximated a line with equation $x=y$.

To aid in determining analytical variability, blanks were run for each leach test, split samples were prepared in each laboratory for analysis in the other laboratories, and standards were analysed for each contaminant.

It was found that, with certain exceptions, reproducibility of the test methods and analytical methods was good. Details of the reproducibility will be presented and discussed with reference to the study objectives.

REFERENCES

(1) EPS Wastewater Technology Centre/Alberta Environmental Centre, "Test Methods for Solidified Waste Characterization", Draft Report, January, 1986.

(2) Porter-Cathcart, N., Friedman, D., Stegemann, J., Wiles, C., and Liem, A., "Overview of a Cooperative Program for the Investigation of Test Methods for Solidified Waste Characterization - Its Goals, Design and Success", Presented at the 4th International Hazardous Waste Symposium on Environmental Aspects of Stabilization/Solidification of Hazardous and Radioactive Wastes, Atlanta, GA, May 3-6, 1987.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

****

WHERE ENTIRE PAPER HAS NOT BEEN INCLUDED IN THESE PROCEEDINGS COPIES WILL BE AVAILABLE IN THE CONFERENCE LOBBY.

THE GENERATION OF HAZARDOUS WASTE BY MSW-INCINERATION CALLS FOR NEW CONCEPTS IN THERMAL WASTE TREATMENT

Paul H. Brunner and Peter Baccini
Dept. of Waste Management and Material Balances
Swiss Federal Institute for Water Resources
and Water Pollution Control
CH-8600 Dübendorf, Switzerland

ABSTRACT

The environmental quality criteria for Municipal Solid Waste incineration comprise air pollution standards and occasionally simple slag properties, but do not specify filter-dusts and scrubber liquids which for some nations are the largest amounts of hazardous waste materials. This paper discusses the formation, composition and leaching behavior of filter-dusts from MSW-incinerators. The following conclusions are drawn: The new goals of the overall incineration process should be the complete mineralization of the organic carbon, concentration of toxic elements in the filter-dust and scrubber sludges, and immobilization of the hazardous elements contained in dust and sludges. The paper includes general quality criteria for the products of incineration.

INTRODUCTION

In highly industrialized and densely populated countries, incineration has the potential to become the most important process for the treatment of municipal solid waste (MSW). By combustion, 1 kg of MSW is converted to approximately 700g off-gas, 270 g slag and 30 g filter-dust and/or scrubber sludge, thus leaving about one third of the initial MSW as a new waste material for disposal by landfilling. While the constituents of the off-gas are regulated in most countries by air pollution standards, quality criteria for slag and filter-dust have not received the same attention yet. Since filter-dust and slag contain leachable heavy metals and refractory organic compounds, these materials require treatment before their ultimate disposal in landfills. The treatment necessary to achieve a non-hazardous quality of these products depends upon the composition of the MSW and the design and the operating conditions of the incinerator. Therefore, modern incinerators have to be optimized not only towards maintaining air pollution standards but also towards the production of solid materials which are well suited for further treatment and ultimate disposal.

PURPOSE

Research is needed to elucidate the genesis, the composition and the behavior of the solid products of incineration. The thereby gained information should serve as a base to define the new objectives of MSW incineration. A new conceptual approach to MSW incineration may eventually lead to improved design and new operating techniques for incineration plants.

The two main purposes of this work are

- to assess the importance of the incineration of MSW as a source of hazardous solid waste products and
- to define new objectives for the incineration of MSW, in order to get incineration products which can be disposed of safely.

APPROACH

Survey of hazardous waste

In order to assess the importance of the hazardous waste produced by MSW incineration, a survey of waste materials was accomplished for a highly developed, mixed residential and industrial region with 1.2 million inhabitants and an area of 1700 km^2 (the Canton of Zurich, Switzerland). The figures collected in this survey were compared with the mass of filter-dust and slag produced by the six incinerators which treat most of the municipal solid waste generated in this area.

Analysis of the solid products of incineration

Slag and filter-dust samples from four Swiss MSW incinerators were analyzed for metals and non-metals. The procedures for sampling and analysis are given elsewhere [1]. To examine the leaching behavior of the filter-dust, samples were:

1. leached by deionized water for 52 hours, with analysis of the concentration of dissolved elements after 0.5, 5 and 52 hours leaching time, and

2. leached consecutively for 14 days by deionized water in intervals increasing from 30 seconds to 2 days. This procedure, introduced by the US-EPA as "Uniform Leach Procedure" to determine the diffusion coefficients of solidified wastes, is described in detail in [2].

The leaching behavior of the slag was not tested by laboratory experiments but was assessed by the investigation of slag deposits (temporary storage, road constructions, and landfills). Leachates in such deposits were collected from lysimeters and drainage systems and analyzed as received.

Effect of incinerator design on product quality

In order to examine the effect of incinerator design and operating conditions on the quality of slag and filter-dust, incinerators with different product qualities were compared. Sampling and analysis of the products of incineration are given in [1]. The elemental composition of the MSW incinerated was calculated from the products of incineration: The sum of element quantities in the off-gas, the filter-dust and the slag equals the mass of this element in the MSW.

PROBLEMS ENCOUNTERED

The composition of the materials investigated in this work (MSW, flue-gas, filter-dust and slag) is heterogeneous and varies with time. It is therefore necessary to collect numerous samples in order to derive conclusions of statistical significance.

Since MSW and slag are materials composed of many compounds covering the entire range of elements and having particle sizes from 10^{-4} to 10^{0} m, these materials are not suited for small-scale laboratory experiments. Therefore, it proved to be necessary to collect the data from full-scale municipal incinerators.

It was not possible for us to vary the operating conditions of the investigated incinerators. Therefore, it was necessary to study various incinerators with different operating and design characteristics in order to examine the influence of incineration on product quality. The conclusions drawn from the comparison of the various incinerators have to be confirmed by further work in an incinerator where operating conditions can easily be manipulated.

RESULTS

Contribution of MSW incineration to the overall production of hazardous wastes

From the survey of wastes generated in the region (Table 1), it is concluded that filter-dusts from MSW incinerators can be quantitatively important amounts of hazardous waste materials. Of course, regional differences in industrial and waste management practice determine the exact contribution of each activity to the production of hazardous wastes but nevertheless, the fact that for a modern, highly-developed, mixed residential and industrial area

	type of waste (as received)	t/year	kg/capita · year
A	.sewage sludge (with 5 % dry matter)	650,000	560
	.municipal solid waste	500,000	430
	.slag from MSW incinerators	160,000	140
B	.filter-dust from MSW incinerators	11,000	10
	.slag from aluminium recycling	5,300	4.6
	.filter-dust from aluminium recycling	1,000	0.9
	.waste oil	5,000	4.3
	.mixtures of oil with soil, water, and sludge	6,300	5.5
	.acids and dyes containing metals	2,600	2.3
	.sludges containing metal hydroxides and pigments	1,200	1.0
	.lead from battery recycling	460	0.4
	.solvents (halogenated)	300	0.3
	.solvents (others)	420	0.4
	.others	∿1,000	0.9

Table 1. Survey of waste materials generated in a region of 1.2 million inhabitants and 1,700 km^2 area (Canton of Zurich, Switzerland). A: wastes generally regarded as non-hazardous, B: products generally regarded as hazardous wastes. (Agricultural wastes are not included).

Element	slag		filter-dust		ore		earth crust [3]
	[g/kg]	EF	[g/kg]	EF	[g/kg]	EF	[g/kg]
Si (as SiO_2)	360-460	1.5	230-320	1	-	-	280
Al	80-180	1.6	60-120	1.1	250-350	3.7	82
Ca	25-100	1.5	30-90	1.5	-	-	41
Na	10-60	1.5	20-80	2.1	400	17	24
Mg	6-18	0.5	28-40	1.5	10-30	0.9	23
K	5-20	1.2	12-74	4.1	-	-	21
Fe	40-230	2.4	28-40	0.6	300-600	8	56
Ni	0.3	3.8	0.2-0.3	3.1	4-55	380	0.08
Hg	0.0001	1.3	0.002-0.014 1)	100 1)	2	25000	0.00008
P	7-14	9.5	1-12	6	200	180	1.1
S	2-4	12	20-40	120	-	-	0.26
Cl	3-6	35	40-78	450	600	4600	0.13
C	15-40	140	14-36	250	850-950	4500	0.2
C-carbonate	7-15	-	1-5	-	-	-	-
Loss on ignit.	10-80	-	10-40	-	-	-	-
Cu	1-4	41	1-5	50	10	170	0.06
Cr	1-10	55	0.5-1.7	11	350	3500	0.1
Zn	4-15	140	13-39	370	40	570	0.07
Pb	1-17	750	6-12	750	50	4200	0.013
Cd	0.03	150	0.2-0.6	2000	4.4	22000	0.0002

Table 2. Concentrations of elements in filter-dust and slag from MSW incineration, and concentrations in ores and the earth crust.[EF: enrichment factor, defined as concentration in the product divided by the concentration in the earth crust]. 1) in sludges from wet scrubbers, the concentration of Hg was found to be 1.3-3.0, EF 27,000.

where most of the MSW is being incinerated, the filter-dust from such incinerators is the dominant hazardous waste, may be encountered in the future in other regions, too.

Chemical properties of slags and and filter-dusts

In Table 2, the range of the composition of the slag and filter-dust is compared to ores and the earth crust. For many elements (e.g. Fe, Si, Al, Ca, Na, Mg), the concentration in the slag and filter-dust approximates the concentration in the earth crust. Some heavy metals and non-metals are highly enriched in the slag and especially in the filter-dust (e.g. Zn, Cu, Cd, Hg, Cl). Although a few of the metals (e.g. Mg, Zn) are as concentrated in the slag and filter-dust as in the ores, it is not yet economically feasible to recycle these metals. This is due to the limited amount available compared to the total production, and the abundant impurities in the products of incineration.

During incineration, the elements in MSW are transferred to the slag, the filter-dust and the flue gas according to their chemical and physical properties [1]. Volatile metals and non-metals are evaporated from the grate and condensed during gas cooling. The chemical speciation of the elements as well as the operating conditions of the furnace, gas cooling and cleaning are important factors in the control of the flux of the elements. Thus certain elements lide Cd, Hg and Cl become highly enriched in the filter-dust. Some of the metals in this product and the flue gas are in part present as chlorides (e.g. $CdCl_2$, $HgCl_2$). of the leachate increased, due to the transformation of alkaline oxides to hydroxides, resulting in a decreased leaching of heavy metals. By the addition of alkaline binders such as cement, the initial leaching of some elements can be decreased also. Care must be taken not to apply too much alkaline material in order to prevent the dissolution of Pb, Zn and other metals at high pH-values, due to the formation of soluble hydroxo complexes.

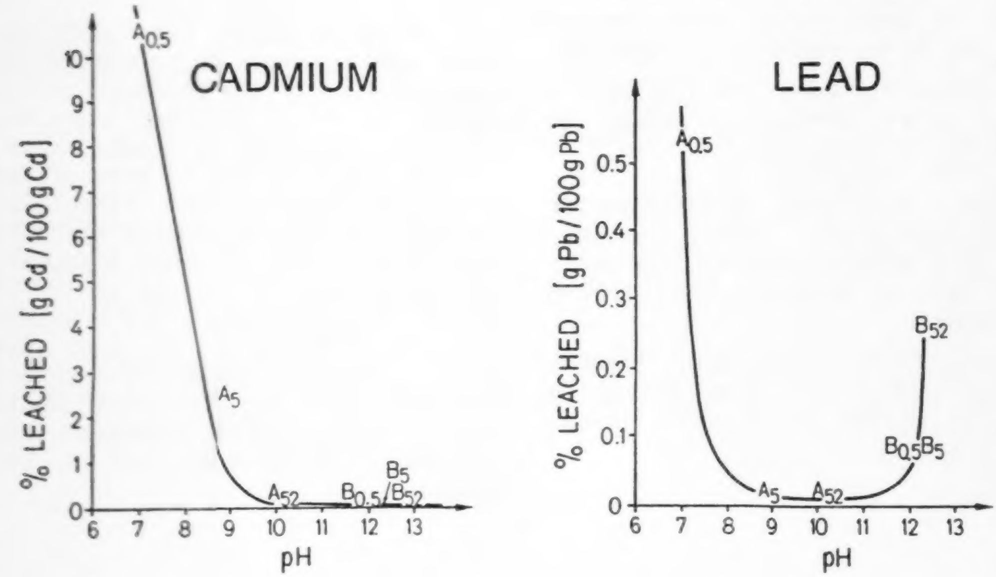


Figure 1. Leachability of cadmium and lead in filter-dust samples for 0.5, 5 and 52 hours leaching time. A: untreated filter-dust, B: filter-dust solidified with cement 1:1

This is in contrast to the compounds in the slag, which consist mainly of oxides. This difference in the speciation is responsible for the difference in solubility of the metals present in slag and filter-dust:

Contrary to the slag, some metals in the untreated filter-dust proved to be highly soluble (Figure 1): At first contact with water, 10% of the Cd and 0.5% of the Pb in the filter-dust are dissolved. With increasing leaching time, the pH-value

Various leachates from deposits of slag were taken from incinerators, intermediate storage areas, landfills of different ages and road constructions. For all leachates, the pH-value decreased with increasing age of the slag deposit (Figure 2). This may be due to the neutralization and leaching of alkaline material by the acid rain, the acidification of the slag by CO_2 from the atmosphere, and from the microbial decomposition of the organic carbon in the slag. It has not been examined yet if the pH-value of such a slag deposit may eventually drop to a value where heavy metals will be dissolved in significant amounts.

Procedures for the handling of MSW incineration products

There are three possibilities to prevent the leaching of metals and non-metals from the deposits of filter-dust and slag:

1. To exclude a water flux through slag and filter-dust in a landfill.

2. To treat the dust and slag chemically before ultimate disposal in order to produce compounds with a low water solubility (e.g. oxides, sulfides, silicates, glassified or sintered products). Thus, the contact with water leads to leachates which have no adverse effect on the environment.

3. To optimize incineration towards the production of materials which are well suited for disposal in sanitary landfills.

The first proposal can be realized either by constructing a water impermeable envelope around a surface disposal or by depositing the product in a deeper geological layer. The latter approach is analogous to the final deposition of radioactive material and is very costly. The first approach is just an intermediate solution and postpones the problems to the period (after decades or centuries) when the envelope becomes water-permeable.

Based on todays experience, it seems more appropriate to change the chemical form of the products of incineration (e.g. so that they are not to be mobilized by landfill leachates), than to try to prevent the access of water to these materials. In order to form a product which is well suited for ultimate disposal, the slag must be washed prior to landfilling. The metals and leachable non-metals in the filter-dust have to be chemically immobilized before disposal, and organic constituents may require a further treatment (recycling of filter-dust back to combustion).

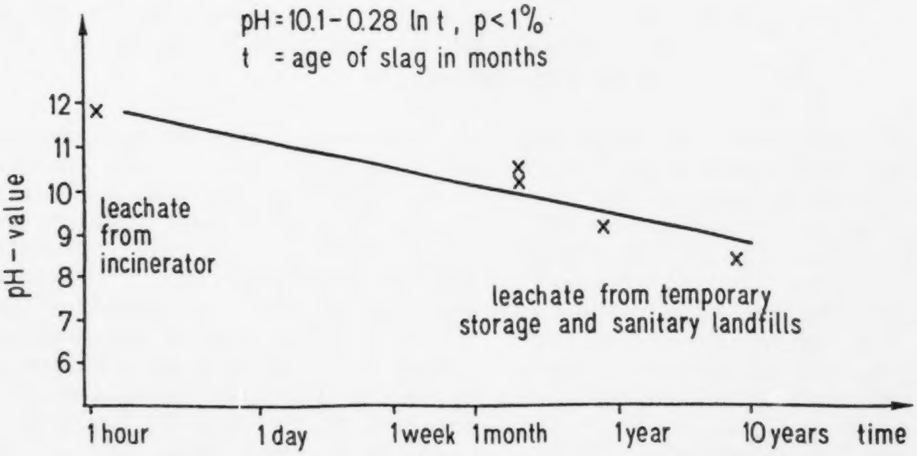


Figure 2. The pH-value of slag leachates decreases with time

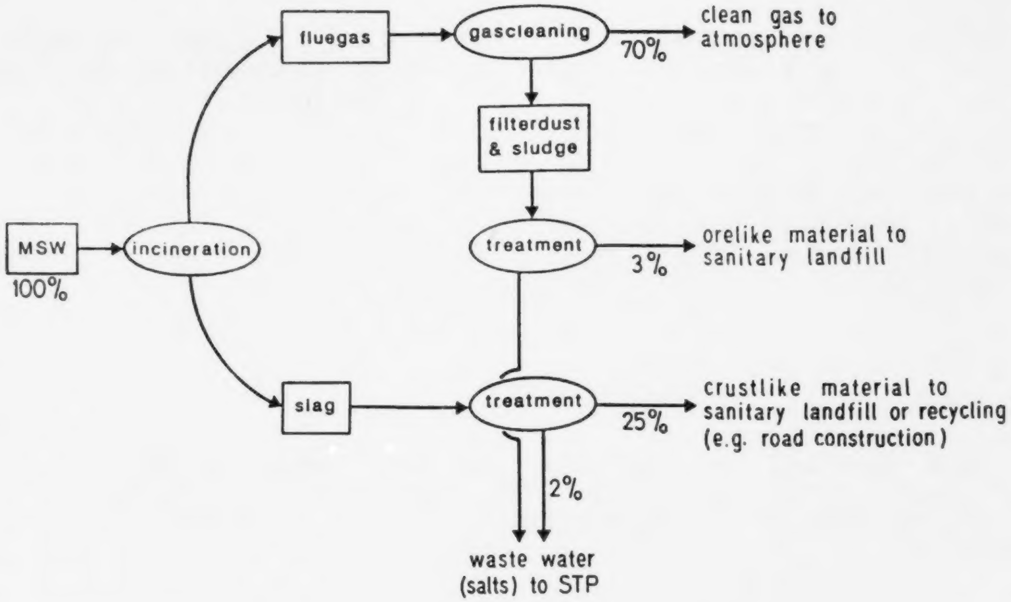

fluegas
gascleaning
70%
clean gas to atmosphere
filterdust & sludge
MSW
100%
incineration
treatment
3%
orelike material to sanitary landfill
slag
treatment
25%
crustlike material to sanitary landfill or recycling (e.g. road construction)
2%
waste water (salts) to STP

Figure 3. Treatment and ultimate disposal of the products of MSW incineration

The third possibility needs further research into the chemistry and physics of incineration. Investigations of the incineration of MSW have shown that it might become possible to design and operate incinerators in such a way that certain metals are concentrated in the slag and others in the filter-dust [1]. As a new objective of incineration, leachable heavy metals and hazardous compounds should be concentrated in the filter-dust, which equals only 2-4 % of the initial MSW, resulting in a relatively clean slag (30 % of MSW). to minimize the leachability of the slag, the combustion should be optimized towards complete mineralization, resulting mostly in metal oxides.

Conclusions

General quality criteria for solid products of MSW incineration could look as follows (Figure 3):

Slag: Earth crust quality, achieved by optimizing incineration and washing of the slag, ultimate disposal in a sanitary landfill or possibly in a road construction.

Filter-dust: Ore-like quality, non-leachable metals due to chemical treatment, disposal in a "mono"-sanitary landfill where contact with other waste materials is excluded.

ACKNOWLEDGMENTS

The contribution of H.P. Diener, H. Moench and R. Zimmerli to analysis and mass balances is especially appreciated. We thank Mrs. H. Bolliger for the grafics work.

REFERENCES

1. Brunner, P.H., and Moench, H., 1986, The Flux of Metals through MSW Incineration, Waste Management and Research, Vol. 4, pp. 105 to 119.
2. US EPA, 1982, Guide to the Disposal of Chemically Stabilized and Solidified Wastes, SW 872, Washington DC.
3. Krauskopf, K.B., 1967, Introduction to Geochemistry, Mc Graw Hill, New York.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

INCINERATION OF PCB'S IN FRANCE

DECONTAMINATION OF ELECTRICAL EQUIPMENT AND POLLUTED SITES

G. MILLOT - PECSIE -
SALES, RESEARCH & DEVELOPMENT MANAGER
AND
GEORGES MILLERET - TREDI -
TECHNICAL MANAGER

PECSIE
B.P. 205 - 95523 CERGY PONTOISE - FRANCE -

TREDI
B.P. 1324 - 69211 LYON CEDEX 03 - FRANCE -

ABSTRACT

During several decades, polychlorinated biphenyls have been extensively used in many countries, but they are now to be burned, because they are considered as too much hazardous chemicals.

Their amount is in France about 100,000 tons and about 100,000 transformers are to be cleaned. The French situation in the area of the toxic waste incineration is reviewed and a description is given of the Saint Vulbas plant, which is the only one authorized in France for the burning of PCB's. It uses a high temperature incinerator (1,200°C), with a quenching section and a wet scrubbing. A description is also given of the unit which has been designed to clean the electrical transformers in the same plant.

1/ INTRODUCTION :

The problem of the environmental contamination by PCB's (polychlorinated biphenyls) is not specific to France ; it is common to all countries using these types of compounds, PCB's have been mainly used as dielectric fluids for transformers and capacitors, hydraulic fluids, and heating fluids as well as in less measure for lubrication fluids, cutting oils, plasticizers, etc.

Their high stability to temperature and fire is the main reason for their extensive use. However, since 1960, contamination of the environment by PCB's has become identified as a major concern, moreover, many accidents (mainly fires on transformers) have revealed hazardous by-products of PCB combustion such as PCDD's (polychorinated dibenzo-p-dioxins) and PCDF's (polychlorinated dibenzofurans) ; TCDD toxicity can be 10^5 times more than that of PCB.

Consequently, the different governments have proposed newregulations. In France, a law datedJuly 8 1975 has limited the use of PCB's to closed systems (transformers, capacitors, heating systems, hydraulic systems). Then a directive from the EEC (European Economic Community) dated October 1st 1985 has forbiden the sale of equipments containing PCB's from June 30 1986. In France, the users are obliged to declare every piece of PCB equipment and to provide them with safety devices like fire protection, electrical protection, and basins to recover the PCB in case of leakage.

A program has been initiated to destroy all existing PCB's and to decontaminate metallic equipment polluted by PCB's before it goes to a landfil. In the French case, about 4,000 tons/year of PCB's were produced and used intransformers during the ten years between 1975 and 1984 ; the annual rate before 1975 was about 3,000 tons. A total of some 100,000 tons of PCB existing and 100,000 transformers need to be treated.

2/ THE SITUATION OF TOXIC WASTE INCINERATION IN FRANCE :

Today, more than one half of the toxic organic waste is incinerated by four plants owned by TREDI (Traitement Revalorisation Elimination de Déchets Industriels). This operating company is able to burn about 200,000 tons/year of organics and its mother company, EMC Group (Entreprise Minière et Chimique) has recently created an engineering company PECSIE (Projets Etudes Conseils Services Industrie Environnement), whose purpose is to develop new processes in the waste disposal area and to market technologies which have been developed and used by TREDI in its plants during the last fifteen years (the first of them was built in 1973).

3/ THE FRENCH PCB INCINERATION PLANT-SAINT VULBAS :

This plant is located about 25 miles from Lyon (France). It was built in 1976 as a plant to incinerate highly- chlorinated products, in liquids, solids, and paste-like form. In 1981, it was authorized by the French Administration to burn PCB's. There is no other plant in France authorized to burn PCB's. Many developments have been made in this plant since 1976, either in the process conditions or in the control and safety areas. At the time of the start-up, a wet scrubbing with caustic soda neutralization system was used. It has since been replaced by an arrangement using acid water loop and a neutralization with lime which is more economical.

The current system consists of :

- an incineration unit of 25,000 tons/year capacity, which includes PCB's (6,000 tons/year) ;
- a decontamination unit for transformers and capacitors whose capacity is 6,000 transformers/year.

A study is now in course to get early authorization to increase the incineration capacity from 25,000 tons/year to 30,000 tons/year

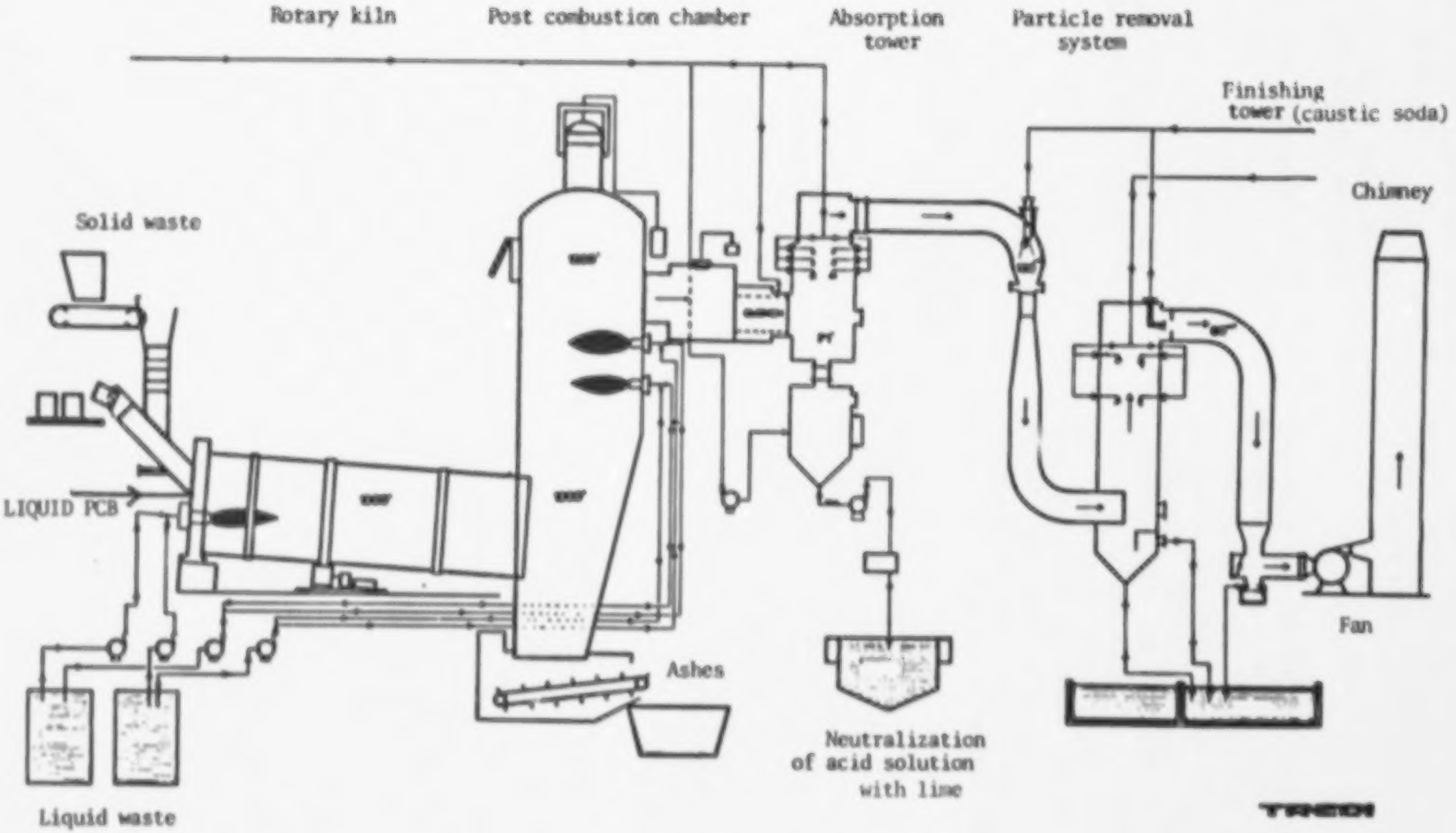

Rotary kiln
Post combustion chamber
Absorption tower
Particle removal system
Finishing tower (caustic soda)
Chimney
Solid waste
LIQUID PCB
Fan
Ashes
Neutralization of acid solution with lime
Liquid waste

Figure N° 1 - High chlorinated waste incineration plant - Saint Vulbas - France - Simplified flow sheet

4/ BASIC PRINCIPLE OF THE PROCESS USED TO INCINERATE PCB's AND HIGHLY-CHLORINATED PRODUCTS IN THE SAINT VULBAS PLANT (See Fig. 1) :

Wastes to be burned are received in large bulk as well as in barrels or other containers. They are introduced in the front face of a rotary kiln that is maintained at about 1,000°C (1,882°F) in the central zone. Liquids of high heating value are stored separately from the low heating value liquids. The two are mixed in such a ratio that the temperature in the furnace can be maintained at the required level.

Liquid PCB's are stored and injected separately from the other wastes. Solids are admitted in the furnace through a hopper and a vertical lock. At the opposite side of the rotary kiln, ashes are recovered in a water pit and gases enter a secondary combustion chamber where the temperature is maintained at 1,200°C (2,192°F) by burning propane.

At the upper of this chamber, the flue gas with a high content of HCl enters a quenching section where its temperature is decreased over a 4 feet length to about 80°C (176°F). This quench favors a maximum concentration of HCl and a minimum of Cl_2 which is less well absorbed by water. The Deacon equilibrium reaction for this condition shows :
$4\,HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2 - 20{,}8\ Kcal$
Following this quenching section, there arethree columns : one for absorption of HCl with water and drawing out of a part of the flow rate of the acid water loop, one with a venturi for the recovery of particles and one for a final neutralization of hydrochloric acid with caustic soda.

The specific conditions required by the regulation for the incineration of PCB's in this unit are :

. a maximum flow rate of 1.5 ton/hour of PCB burned

. 20 % of excess air at the chimney 1,200°C (2,192°F) for the temperature in the secondary chamber

. compliance with the emission standards (see below)

5/ STANDARDS TO BE COMPLIED WITH AND RESULTS :

PCB EMISSIONS	REQUIRED VALUES		MEASURED VALUES
	Instantaneous concentration	maximum flux	
Liquids	1.5 mg/Kg	1.2 Kg/day	0.035 mg/Kg
Solids	15 mg/Kg	-	10.00 mg/Kg
Gas	1 mg/Nm^3 *	1.0 Kg/day	0.01 mg/Nm^3

* Nm^3 = standard cubic meter at 1 atm and 0 degré C.

Independently of PCB, the plant is required to comply with the normal emission standards. In particular, the flue gas released to the atmosphere must be in accordance with the following limits :

	Maximum instantaneous concentration (mg/Nm^3)	Maximum flux (Kg/day)
Hcl or Cl_2	100	120
Particles	150	100
Unburned material	5	6
Heavy metals (total)	5	6
Pb, Co, or Hg	0.1	-
SO_2	100	235
CO	200	12
F	5	6
NO_x	200	235

The checking of these limits is made every day by the laboratory of the plant and periodically by an external laboratory. The levels recently obtained for HCl and particles are 30-50 (maxi 100) and 100-120 (maxi 150) respectively. Generally speaking, the efficiency of the flue gas cleaning system is higher for HCl than for particles. This is normal for a wet scrubbing system. In other plants where the particles limitation is lower (50 mg/Nm^3 for instance), the use of bag filters give levels as low as 10 mg/Nm^3.

6/ TECHNICAL EVALUATION AND GENERAL ACCEPTANCE OF THE PLANT :

This plant has been run with PCB's for about now 7 years, under the close control of the French Administration which is informed in detail about the wastes burned and the results of the environmental measurements related to water, air and solids. Improvements have been made in many areas and particularly relative to the protection systems. Also the employees of the plant are given periodic medical examinations. No anomalies have been observed concerning the health of the people working in the plant. No accident has been noted concerning PCB activity. About the acceptance by the people living around the plant, the closest village is located at about 1 mile away and the plant is situated in an industrial area intended to accept such a type of industry. Many degrees of information are available for the public and some "open-door" days have been organized in order to maintain a climate of confidence between the operating management of the plant and the population of the neighboring villages and towns.

7/ BASIC PRINCIPLE OF THE PROCESS USED TO DECONTAMINATE PCB POLLUTED ELECTRICAL EQUIPMENT (TRANSFORMERS AND CAPACITORS) (See Fig. 2) :

In 1984, an extension was made of the basic incineration activity of the Saint Vulbas plant by designing a plant to clean electrical equipment after it has been drained of PCB's. The process uses an autoclave under vacuum and a solvent which is able to dissolve PCB which remains on the metallic surfaces of the equipment after draining.

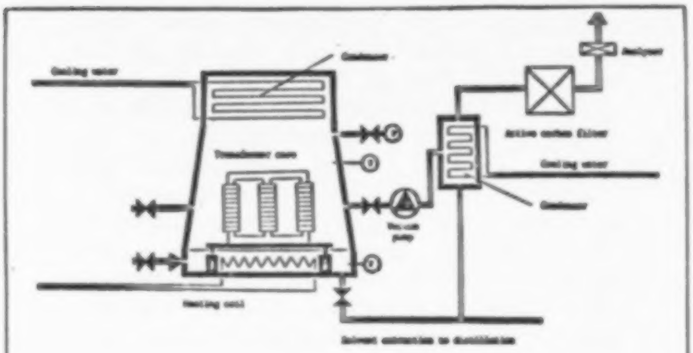


Figure N° 2 - Decontamination of PCB polluted electrical parts
Simplified flow sheet

Only porous materials (such as wood) are not processed and are directly burned in the furnace. Solvent is evaporated inside the autoclave and condensed at the upper part by providing "a rain" of liquid solvent washing the metallic parts. A part of the solvent is condensed inside the parts themselves, which gives a high efficiency for the recovery of PCB. The solvent is continuously distilled from the PCB which then is burned in the incineration plant.

Six autoclaves are now running an are connected to the same system of heat production and solvent distillation. The capacity of the unit is now 6,000 transformers/year.The PCB content of the equipment at the end of a cycle of decontamination less than 100 ppm which is considered in France as the limit for the non-PCB materials authorized to go to landfil. Tests will be carried out in a near future in order to check the availability of the equip-ment to obtain clean equipment ready for refilling with another dielectric fluid.

8/ DEVELOPMENTS FOR THE DECONTAMINATION OF POLLUTED SITES

Besides the two main activities described above (incineration of PCB's and decontamination of electrical equipment), we are now developing in-situ services in case of "cold" accidents or "hot" accidents associated with PCB equipment. In both cases, we propose :

- inspections and analysis of the contaminated sites by qualified people in order toget an accurate assessment of the contamination ;
- in-situ processes like decontamination of polluted soils (now under development). Studies have proved the interest in the economics of such a process compared to the transportation of oil to the incineration plant, some by-products polluted by PCB being only burned in that plant ;
- assistance for the reestablisment of the non-contaminated status of an area.

In another area, we are now developing processes to decontaminate mineral oils polluted by PCB. A large number of mineral oil transformers are, indeed, polluted at a level above 100ppm and the PCB content has to be decreased from levels around 1000-2000 ppm to under 100 ppm.

Such operations are planned in-situ and will generate some PCB by-products which subsequently will be burned in the Saint Vulbas incineration plant.

9/ CONCLUSION :

With the help of the PCB incineration plant of Saint Vulbas, France is now solving a large part of the problems related to the new regulations concerning PCB's : firstly, the replacement of PCB equipment with new equipment ; secondly the incineration of PCB products resulting from potential accidents with PCB equipments ; and thirdly, the cleaning of the mineral oil transformers which has been polluted by PCB. In any case, the decision which was made to authorize such a plant in 1980 has been proved to be an effective one. An incineration unit is indeed the best compromise for the safe destruction of PCB. This does not mean that other technologies should not be developed for the near future as alternatives to incineration. We are working on them too.

Disclaimer

The work in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

ENGINEERING ANALYSIS OF METAL EMISSIONS FROM THERMAL DESTRUCTION DEVICES

R.G. Barton
W.D. Clark
W.R. Seeker

Energy and Environmental Research Corp.
18 Mason
Irvine, CA 92718

C.C. Lee

USEPA
Hazardous Waste
Engineering Research Lab
26 W. St. Clair St.
Cincinnati, OH 45268

ABSTRACT

Some toxic metals present in hazardous waste streams can vaporize when incinerated. These metals concentrate in small particles which are difficult to remove from the flue gas and are easy to respire thus presenting a potential health hazard. This paper discusses the mechanisms of the process and describes a modeling procedure currently under development to predict metals emissions. The approach is based on equilibrium speciation and evaporation of metals at the local conditions in the combustor along with flyash entrainment, nucleation and condensation of vaporized species, and particle removal by air pollution control devices. The model is applied to a municipal solid waste incinerator and good agreement is achieved between predicted and measured metals emissions. Sensitivity of vaporization and emission of metals to the conditions which exist in the burning waste bed and to the chlorine content of the waste is examined in a rotary kiln/electrostatic precipitator incineration system. Vaporization of metals is found to increase with increasing burning temperature and waste chlorine content and with decreasing stoichiometric air ratio. Partitioning of volatile metals between fume and flyash is found to depend on the identity of the nucleating species and the ratio of the surface area of the fume to the flyash. Volatile metals such as mercury, lead and barium are found to be concentrated in the submicron fume particles which are most likely to escape into the atmosphere.

INTRODUCTION

Emission of toxic metals from hazardous waste incinerators presents a potential health hazard of increasing interest to state and federal regulatory agencies. Particles in the size range which can escape removal by air pollution control equipment (typically

Preceding page blank

submicron) are also those that can be inhaled. If these fine particles contain toxic metals they can pose a very serious health risk. The U.S. Environmental Protection Agency (EPA) has drafted proposed regulation for restricting the burning of metal-bearing wastes in boilers and industrial furnaces based on dispersion modeling and worst-case risk assessment (7). Similar regulations or guidelines may be forthcoming for hazardous and municipal waste incinerators. A means of estimating the quantity and size distribution of metals emissions from thermal destruction devices would greatly aid in design, permitting and regulating incinerators to prevent emissions.

The fate of metals during the combustion of metal-bearing waste streams is illustrated in Figure 1. Metal-containing waste compounds dry and devolatilize, then burn in a locally oxygen-depleted atmosphere. Inorganic inclusions are exposed to a high-temperature reducing environment where, depending on the local conditions, metals may be converted into more thermodynamically stable forms including oxides, chlorides or pure metals. Volatile species vaporize in the active combustion zone and are carried away with the combustion gas. As the combustion gas cools, the volatile metals condense on the surfaces of existing particles or, if sufficiently supersaturated, nucleate into new superfine fume particles. These fume particles grow with further condensation and coagulation into submicron particulate. Non-volatile metals typically end up as residual ash or entrained fly ash, whereas volatile metals are partitioned between flyash which is easily

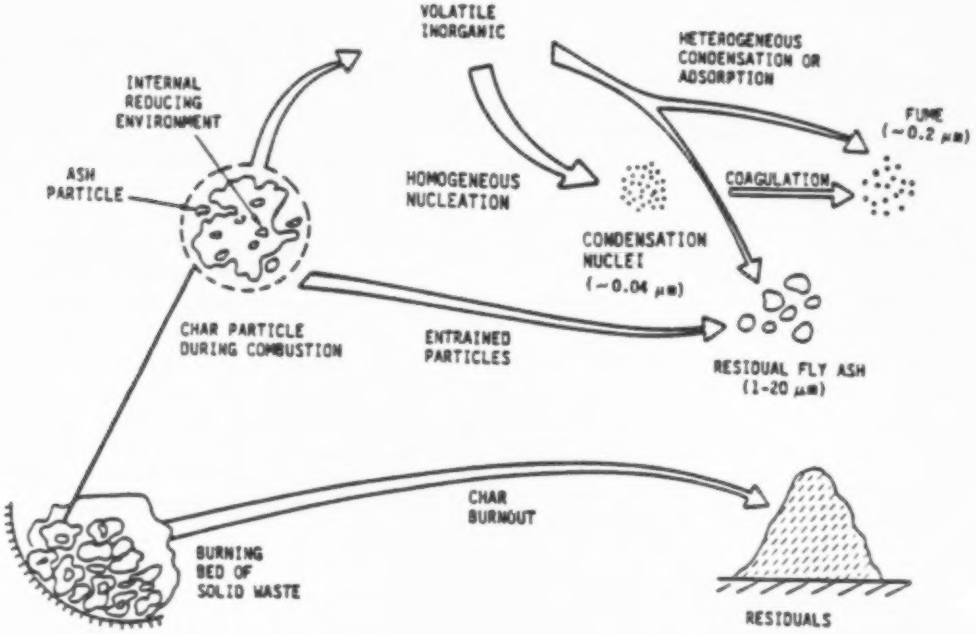

VOLATILE INORGANIC
HETEROGENEOUS CONDENSATION OR ADSORPTION
INTERNAL REDUCING ENVIRONMENT
FUME (~0.2 μm)
ASH PARTICLE
HOMOGENEOUS NUCLEATION
COAGULATION
CONDENSATION NUCLEI (~0.04 μm)
CHAR PARTICLE DURING COMBUSTION
ENTRAINED PARTICLES
RESIDUAL FLY ASH (1-20 μm)
CHAR BURNOUT
BURNING BED OF SOLID WASTE
RESIDUALS

Figure 1. Mechanisms of metals partitioning in waste combustion.

collected by air pollution control devices (APCD) and submicron fume which is much more likely to escape into the atmosphere.

PURPOSE

The objectives of this study are twofold. The first is to examine the feasibility and utility of a predictive approach to characterize metals emissions from thermal destruction devices based on simulations of the controlling chemical and physical processes. The second is to examine the sensitivity of metals emissions to critical design and operating parameters including waste composition, combustion temperature and combustion stoichiometry.

APPROACH

The current modeling approach is illustrated in Figure 2. A detailed heat and mass transfer model is currently under development which incorporates drying, devolatilization, combustion and diffusion in burning beds to predict local stoichiometry and temperature. A more simplified approach is employed for this study which uses bulk temperatures estimated from mass and energy balance as described by Clark et al (1). The impact of stoichiometry and temperature is then examined by varying these parameters. Chemical reactions and phase changes are assumed to be fast and the NASA Equilibrium Code (3) is applied at the local burning conditions for the waste composition to determine the

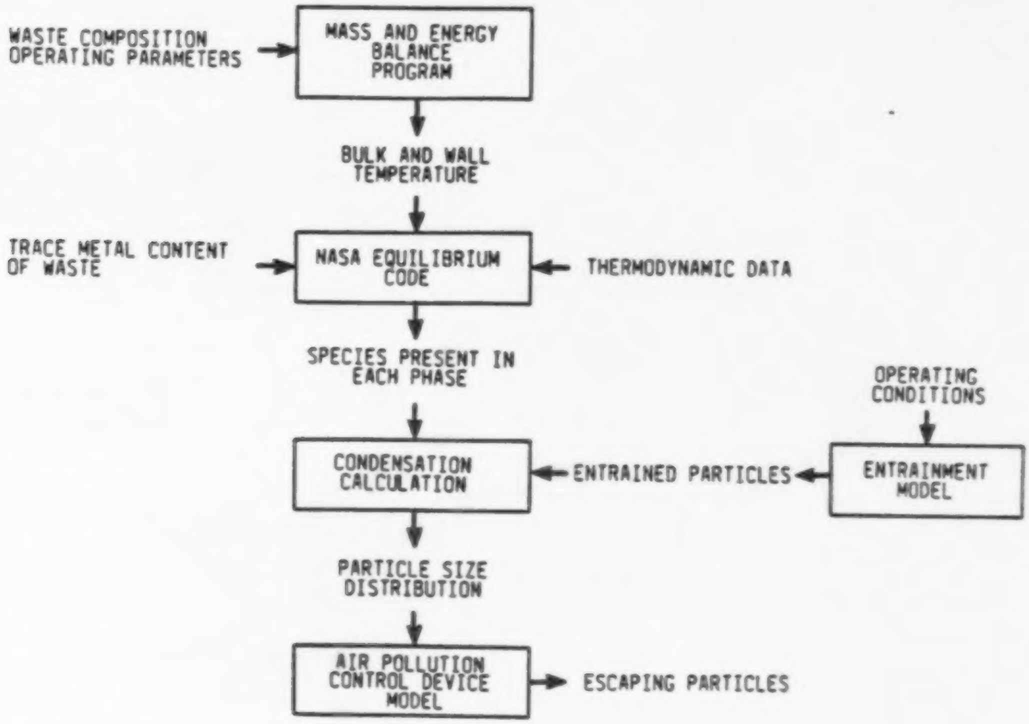

WASTE COMPOSITION
OPERATING PARAMETERS
MASS AND ENERGY BALANCE PROGRAM
BULK AND WALL TEMPERATURE
TRACE METAL CONTENT OF WASTE
NASA EQUILIBRIUM CODE
THERMODYNAMIC DATA
SPECIES PRESENT IN EACH PHASE
OPERATING CONDITIONS
CONDENSATION CALCULATION
ENTRAINED PARTICLES
ENTRAINMENT MODEL
PARTICLE SIZE DISTRIBUTION
AIR POLLUTION CONTROL DEVICE MODEL
ESCAPING PARTICLES

Figure 2. Current approach to metals partitioning modeling.

partitioning of metals between chemical species and phases.

Physical entrainment of particles into the gas stream depends on the solid properties including particle size and density, the gas velocity and properties, and the incinerator design and operating conditions. For rotary kilns, the correlation developed by Li (5) is used to calculate particle entrainment.

As the gas cools, it becomes supersaturated with volatile species. A detailed model describing nucleation, condensation, and coagulation of these species as a function of time, temperature, and particle loading and size distribution is under development following the approach of Friedlander (2). For simplification for this study a less detailed model is used. As the gas cools, the least volatile vaporized species is assumed to nucleate forming 0.04 micron fume particles. These particles provide sufficient surface area to prevent further nucleation and other volatile species are assumed to condense on existing particles, including the fume, in direct proportion to their surface area.

The resulting particles entrained in the cooled flue gas enter the APCD with a wide size distribution of entrained flyash with a coating of condensed volatiles and a single size (typically around 0.2 micron) of submicron fume consisting entirely of condensed volatile metals. Detailed APCD models are available to predict particle collection in scrubbers, filters, cyclones, and electrostatic precipitators (ESP). For this study, only ESP are considered, using the model developed by the Southern Research Institute (6).

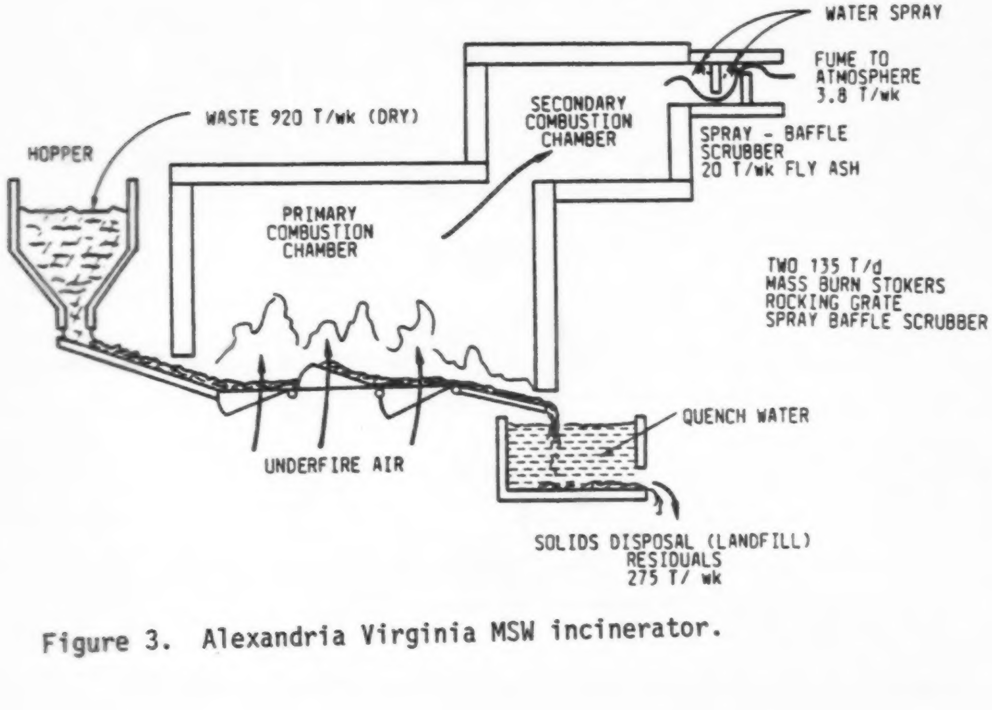

WATER SPRAY
FUME TO ATMOSPHERE 3.8 T/wk
WASTE 920 T/wk (DRY)
SECONDARY COMBUSTION CHAMBER
HOPPER
SPRAY - BAFFLE SCRUBBER 20 T/wk FLY ASH
PRIMARY COMBUSTION CHAMBER
TWO 135 T/d
MASS BURN STOKERS
ROCKING GRATE
SPRAY BAFFLE SCRUBBER
QUENCH WATER
UNDERFIRE AIR
SOLIDS DISPOSAL (LANDFILL)
RESIDUALS
275 T/ wk

Figure 3. Alexandria Virginia MSW incinerator.

Currently there is insufficient data to rigorously apply and verify the model and to justify some of the simplifying assumptions made necessary by the lack of data and by the early stage of development of some of the more sophisticated submodels. In this study the focus has been on determining the limits of successful predictions that can be achieved using the simplifying assumptions. To accomplish this, some unknown parameters were established by fitting the results and then examining the ability of the methodology to reproduce the emissions of other species. Also, the impact of operational parameters was examined by varying the parameters around the baseline conditions.

RESULTS

In order to assess the validity of the modeling approach, the Alexandria, Virginia Municipal Solid Waste (MSW) incinerator was simulated and the results compared with the experimental data obtained by Law (4). The incinerator shown in Figure 3 burns 135 tons per day of paper, trace metals, and other municipal refuse using a rocking grate mass burn design with a spray baffle scrubber to remove large (>10 micron) particles. Insufficient data were available to allow prediction of the amount of material entrained from the bed and the bed's temperature. Accordingly, 19 percent of the ash was chosen as the entrained fraction which reproduced the experimentally determined magnesium concentration. A bed temperature of 1008°K was found to be necessary to reproduce the measured lead concentration. With these assumptions, the concentrations of lead and magnesium in the other emissions streams and the concentrations of other metals in all streams were predicted in good agreement with the measurements. This is demonstrated in Figure 4, which indicates the validity of the equilibrium approach to metals partitioning.

The sensitivity of metal emissions to operating parameters was examined by predicting the performance of a hypothetical 35 MM Btu/hr rotary kiln burning waste fuel oil contaminated with aluminum, iron and trace metals species. Temperature, local stoichiometry, and waste stream chlorine content were determined to have significant effects on the behavior of the metals in an incinerator, as shown in Figure 5. The fraction of any metallic compound which vaporizes depends on its vapor pressure, which increases with temperature. Volatile species such as mercury compounds are easily vaporized at low temperatures whereas more refractory species such as chromium compounds require high temperatures to vaporize. At 1040°K cadmium oxide, a refractory species, decomposes to cadmium metal which is completely volatile at that temperature.

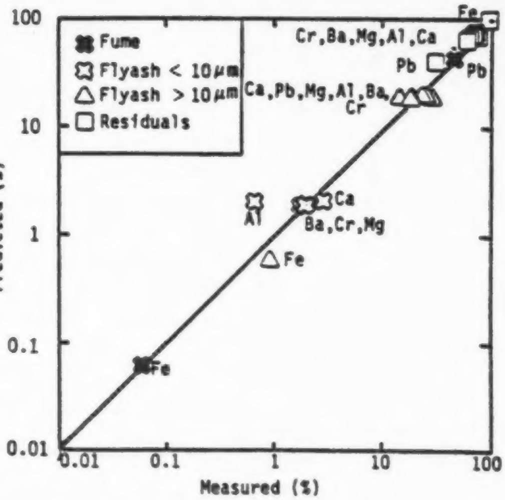


Figure 4. Metals partitioning: ratio of waste to feed flow for each metal.

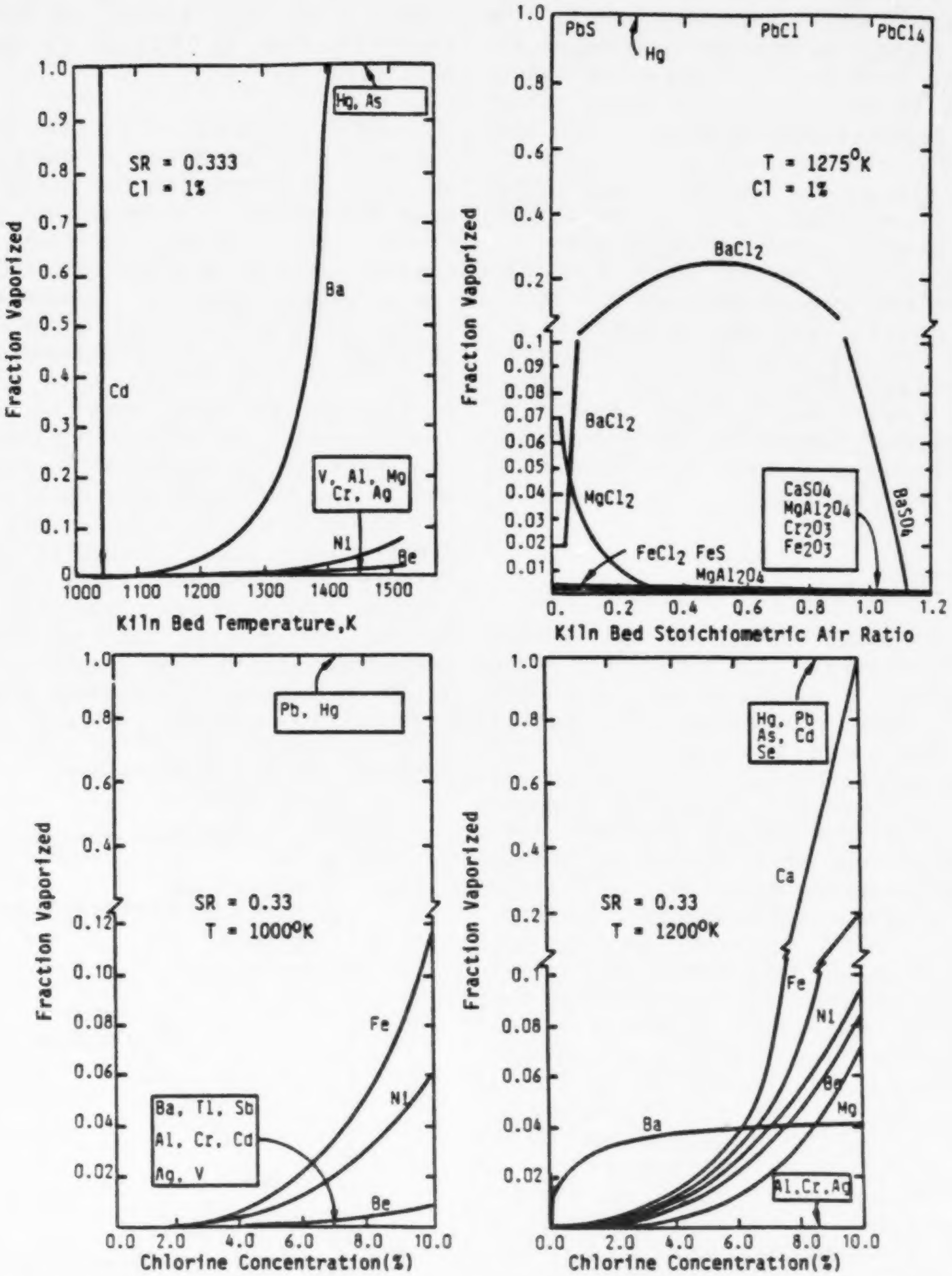


Figure 5. Vaporization of metals species at equilibrium.

The amount of air available at the surface of each burning particle is also important. When the amount of air approaches or exceeds the stoichiometric quantity most of the metals are present in highly oxidized states. As the amount of air decreases the metals tend to form more reduced species. In addition, they shift away from oxides to form chlorides, other halides and sulfides. The chlorides of metals are significantly more volatile than the oxides and vaporize to a greater extent at any given temperature. Thus, increasing waste chlorine concentration increases the amount of chloride formed and increases the amount of metal vaporized.

The entrainment model was used to estimate a flyash loading of 2.6% of the waste ash. A typical size distritution was estimated from data from similar systems having 50% of the mass smaller than 15 microns resulting in a specific surface area of 0.4m^2/g. This represented about 97% of the available surface area for heterogeneous condensation of volatile species, the remainder being homogeneous condensation nuclei. The ESP of the APCD system was predicted to be about 88% effective in removing the submicron fume and 99% effective in removing the flyash. Figure 6 shows the predicted effect of local bed conditions on metals emissions. At lower temperatures, lead was the nucleating species comprising the bulk of the submicron fume. At temperatures above 1100°K barium became the nucleating species resulting in higher emissions. As stoichiometry changed from very rich to fuel lean, the nucleating species

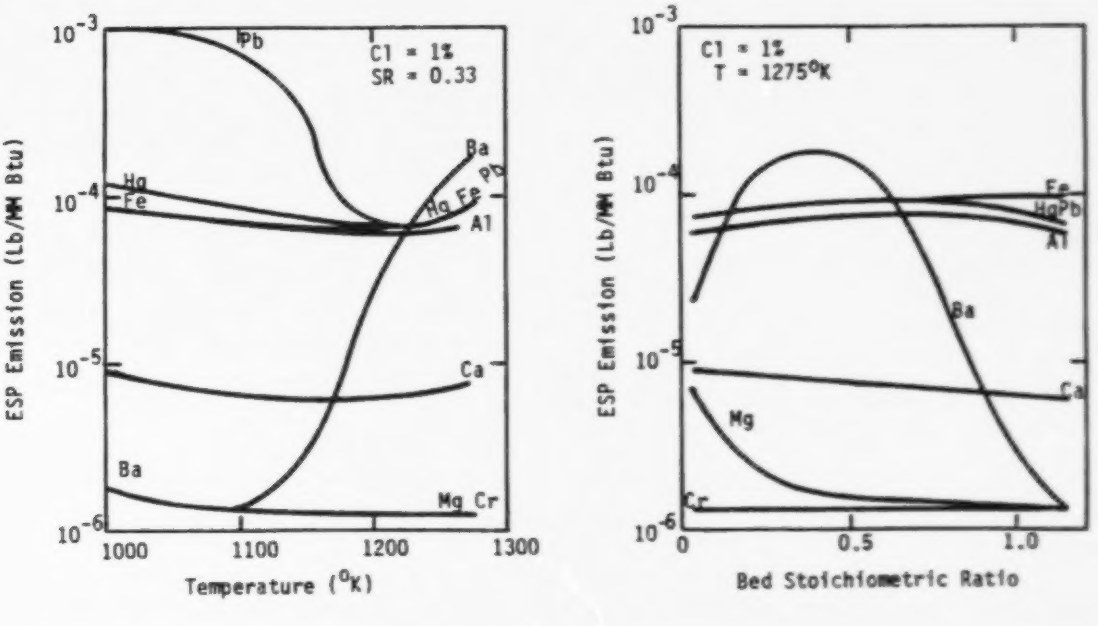


Figure 6. Effect of temperature and stoichiometric air ratio on metals emissions from rotary kiln/ESP.

changed from magnesium to barium to iron. Mercury and lead were present in the condensate and iron and aluminum were present in the flyash in significant quantities under all conditions investigated.

In summary, vaporization of metals tends to increase with increasing temperature and chlorine content and with decreasing availability of oxygen in the high temperature zones. Partitioning of condensing metals between fume and flyash depends on the identity of the nucleating species and the ratio of the surface area of the fume to that of the flyash. Volatile metals can be concentrated in the submicron fume particles which are most likely to escape the APCD and be emitted into the atmosphere.

ACKNOWLEDGEMENTS

This work was performed under EPA contract 68-03-3365, Engineering Analysis of Hazardous Waste Thermal Destruction, with the support of the EPA Hazardous Waste Engineering Research Laboratory and the Office of Solid Waste.

REFERENCES

1. Clark, W.D., W.R. Seeker, and C.C. Lee, 1986, Engineering Analysis of Hazardous Waste Incineration; Energy and Mass Balance, Proceedings of the Twelfth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, EPA-600/9-86-022, pp 360-368.

2. Friedlander, S.K., 1977, Smoke, Dust and Haze: Fundamentals of Aerosol Behavior, John Wiley and Sons, New York.

3. Gordon, S. and B.J. McBride, 1976, Computer Program For Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouquet Detonations, NASA SP-273.

4. Law, S.L. and G.E. Gordon, 1979, Sources of Metals in Municipal Incinerator Emissions, Environmental Science and Technology, Vol. 13, No. 4, pp 432-438.

5. Li, K.W., 1974 "Application of Khodorov's and Li's Entrainment Equations to Rotary Coke Calciners" AICHE Journal, Vol. 20, No. 5, pp. 1017-1020.

6. McDonald, J.R. and A.H. Dean, 1982, Electrostatic Precipitator Manual, Noyes Data Corporation, Park Ridge, New Jersey.

7. USEPA, 1986, Hazardous Waste Management System: Standards for Owners and Operators of Boilers and Industrial Furnaces, Draft, 40 CFR Parts 260, 264, 265, 266, 270, and 271.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

DISTILLATION OF LEACHATES FROM HAZARDOUS WASTE LANDFILLS - ONE YEAR OF EXPERIENCE

Hans-Christian Steinmetzer
Bayerisches Landesamt für Umweltschutz
(Bavarian EPA)
Rosenkavalierplatz 3
D-8000 München 81
Federal Republic of Germany

ABSTRACT

The West German Federal Waste Disposal Act of 1972 sets a general framework with regard to management of waste disposal allowing the states (Länder) substantial liberty in achieving the implementation. Bavaria recognized the need and took on responsibility for proper management of hazardous waste very early. A regionally operating cooperative and a state wide semi-public organization founded in 1966 and 1970, respectively, run central facilities of comparatively high technical and ecological quality, the use of which is basically compulsory.

Although incineration and chemical/physical treatment are given high priority, landfills will remain indispensable. Conventional treatment of their leachates via extraction and separation of heavy metals as insoluble hydroxides or sulfides does not remove the organic contents quantitatively and does not reduce the burden of water soluble salts at all, both of which are finally discharged, at least in part, into the aquatic system despite further treatment of the prepurified leachate in a municipal sewage treatment plant.

On the basis of positive results with a pilot plant, one of the Bavarian hazardous waste treatment organizations installed a leachate concentration facility in May 1986, with the financial assistance of the state of Bavaria. Its basic feature consists of a two stage evaporation process under alkaline conditions for 3.6 m^3 of leachate per day.

First hand experience with this facility is described pointing out several problems encountered, and some ambiguous results. Although the general performance has to be qualified as satisfactory, a couple of problems have still to be overcome. For this purpose, a 2 years research program was initiated including investigation of the suitability of various materials for critical sub-units and on the possibility of treating aqueous hazardous wastes other then leachates.

INTRODUCTION

In common with most western industrialized countries, the Federal Republic of Germany has passed legislation aimed at identifying hazardous wastes and controlling their transport and disposal. From an ecological point of view, high temperature incineration for organic material and physical or chemical treatments for inorganic waste are generally considered preferable to direct land disposal. Nonetheless, secure landfills with multibarrier enclosures and a highly effective leachate collecting system remain indispensable for disposing of the residues of the aforementioned treatment techniques and of other solid inorganic wastes.

A further problem for which we have yet to find a completely satisfactory solution, is the safe disposal of the leachate of hazardous waste landfills. A tentative approach to overcome this difficulty consists of first steam stripping, then concentrating these leachates in a two effect evaporator, thus separating organic and salt residues from the aqueous phase. Volatile organics as well as organic residues are fed into the incinerator for organic hazardous waste which produces the energy for the evaporator.

The salt residues can be disposed of in a landfill under special conditions, thus closing the loop between waste and leachate. A hazardous waste facility could then achieve the goal of producing virtually no (landfill) or only negligible (incineration, chemical/physical treatment) emissions.

Being the largest of the federal states (70.500 sq.km, or 27.200 sq. mi., ca. 11 million inhabitants), Bavaria has a relatively low density of population and industry (of high technological standard) compared to most areas of central Europe. These factors lead to a peculiar mix of advantages, problems and corresponding solutions.

With the creation of a municipal cooperative (ZVSMM: Zweckverband Sondermüllplätze Mittelfranken) working on a strictly regional basis as early as 1966, and the foundation of a state wide semipublic organization (GSB: Gesellschaft zur Beseitigung von Sondermüll in Bayern) in 1970, Bavaria is at the forefront of hazardous waste treatment practices in Germany an beyond its frontiers, and was able, therefore, to shape German federal legislation by presenting practicable solutions. Both ZVSMM and GSB run efficient and technologically sophisticated waste disposal and treatment operations. As a consequence, waste treatment costs are relatively high (landfill: $50 - 150/t: incineration: $180 - 700/t) thus creating a substantial incentive for waste producers to ship their wastes to surrounding states or countries with lower treatment standards and costs. For this reason, waste exports are generally forbidden; the use of the above mentioned facilities is compulsory with only a few exceptions granted for some existing waste treatment sites operated by large companies.

Facilities

The two Bavarian hazardous waste management organizations have integrated treatment facilities consisting of rotary kiln incinerators, chemical-physical as well as water emulsion treatment plants and landfills. Each facility is assigned approximately one third of the total hazardous waste (ca. 400 000 t/year) sent for disposal. ZVSMM runs two hazardous waste landfills; the first (A), with a volume of one million m^3 (1.31×10^3 yds^3), opened in 1966 and is now almost full. Its ground liner consists of compacted clay of varying thickness and quality, the profile of which shows a couple of sinks into which the leachate is collected via an area drainage system combined with perforated gathering tubes from which the leachate is pumped off. At certain stages of development, the landfill was equipped with intermediate clay liners with independent drainage systems. Over all, the structure of Landfill A is a good example of the evolving concepts of security measures for this type of disposal over the last 20 years. Landfill B, with a total volume of 0.8 million m^3 (1.05×10^3 yds^3) which opened in 1985, consists of an artificially compacted clay liner of 2 m (6.5 ft.) thickness with an inclination of 3%. A system of drainage and gathering tubes under the liner is sloped to drain the leachate towards the lowest point of the landfill. In order to meet advanced demands of security, the parts of the landfill scheduled to open in the future will be equipped with an additional high density polyethylene film (HDPE) liner, and a multibarrier leachate gathering tube system which should make repairs much easier.

From the beginning of the Bavarian waste management scheme, it was required that organic wastes must be incinerated instead of landfilled. An exception to this was landfill A of ZVSMM, which had to accept organic waste until the incinerator was completed in 1981. It was recognized very early however that some bending of this rule would be required, since some predominantly inorganic wastes with some organics present (for example, flocculants in plating sludges), or soils contaminated with very low levels of organics could not be economically incinerated and would have to be landfilled. As a result Landfills B of ZVSMM and C of GSB both have organic contaminants in them.

Special precautions are taken with inorganic wastes and residues having high water extractability. Water extractable salts or heavy metals are treated with special care; they are usually encapsulated in special clay lenses, or in drums placed in box-like concrete structures. Highly toxic wastes are placed in a high security below ground landfill, an abandoned salt mine.

Characteristics of the leachates from the three Bavarian landfills are shown in Table 1. The differences in the leachates may be attributed to the aforementioned changing disposal practices and to the fact that the amounts and types of wastes deposited changed both with time, and with the type of products being manufactured while each landfill was in operation. The following sequence of conventional treatments was used on the leachates:

- Mixing the leachate with emulsions in an emulsion separation plant to extract organics, breaking the resulting emulsion and incinerating the organic phase. This is accomplished by acidification and addition of $FeCl_3/AlCl_3$.
- Addition of NaOH and polyelectrolytes.
- Sedimentation and filtration on a precoated rotating drum filter, incinerating the filter cake.
- Send aqueous phase to municipal treatment plant.

One must note that water soluble salts and minor amounts of organics are present in the aqueous discharge sent to the treatment system.

EVAPORATION FACILITY

The volume and characteristics of the wastewater discharged suggested that concentration of the aqueous waste by evaporation would he advantageous. Results of a pilot plant study on this type of leachate, and knowledge that evaporation was widely practiced in the chemical industry prompted ZVSMM to build a leachate concentration facility (LCF) at a cost of about §3.000.000, at least half of which was contributed by the Bavarian state government. The LCF went into operation in May 1986, and was designed to treat 3.6 m^3/h (15.8 gpm) or 21000 m^3 (5,555,000 gal./yr.) of landfill leachate operating on an 3 shift basis. Energy was supplied from steam produced by the hazardous waste incinerator.

A simplified flow sheet of the LCF is shown in Fig. 1. Principal steps in its operation are:

PRETREATMENT

The leachate is made alkaline, and preheated by a graphite heat exchanger before passing down the multiplate steam stripping column. Overhead vapor is condensed, and separates into organic and aqueous phases. Sulfuric acid is added to convert ammonia to ammonium sulfate, which is collected and later batch distilled. The non-condensable fraction of the overhead vapor and the organic phase are sent to the incinerator.

EVAPORATION

In American engineering practice, the unit operations performed here would be called multiple effect evaporation. In this case two effects or stages are used, as illustrated in Fig. 1. Feed from the stripper ist preheated by condensate from the first stage heat exchanger, then is injected into the forced circulation evaporator. Steam at 140° C heats the liquid, and a portion of it is flashed to vapor which passes overhead. The remaining liquid is continously circulated by the pump shown at the bottom of the evaporator body; after the desired concentration is reached, a portion of the liquid is diverted to the second stage. While the first stage operated at atmospheric pressure, this stage is maintained under a partial vacuum (0.75 bar or 7 psia) causing the water to boil at 80°C (176°F), allowing one to use the vapor from the first stage for heating. The corrosive nature of the feed requires that both of the heat exchangers be made of graphite, and the vessels and pumps of Hastelloy ^{R} C. The exhaust from the vacuum pump and tank vents are passed to the incinerator. Distillate quality is such that it can be used for other purposes in the integrated hazardous waste facility.

Solid Residues

A tube pump removes solid containing concentrate from stage 2 continuously. After dewatering in a decanter, the nearly dry crystalline solid is transferred automatically into large bags which are deposited in a clay lense in Landfill A. This should minimize the chance of reextraction into the leachate.

NEGATIVE ASPECTS

General

The LCF has not been able to run continuously and at full capacity due to two major factors: insufficient quantities of steam (which should be corrected when installation of a new incinerator is completed) and lack of adequately trained manpower. As new problems arise, we shall point them out, to demonstrate the difficulties inherent in introducing a new treatment technology.

Pumps

The majority of unscheduled shutdowns were due to pump failures. In particular, silicate type packing rings were attacked by the concentrated alkaline leachate and salt residues. Replacement of the packings with the new carborundum fiber type is expected to overcome this problem.

Foaming

Frequently, under certain conditions, violent foaming of the boiling liquid in both evaporator stages occur. Carrying liquid over by the foam then contaminates the distillate, requiring reprocessing an entire batch unless caught early enough. The amount of foam appears to be related to the extent of scale formation on the evaporator surfaces, since immediately after they are cleaned, much less foam is apparent. ZVSMM is experimenting with different types of antifoam agents, but none has been completely satisfactory. In addition, the antifoaming agents are suspected of increasing TOC of the distillates by being partly carried over the vapor.

Scaling

Scale formation in the stripping column consists mainly of precipitated carbonates, which can be easily removed by flushing the column with amidosulfonic (sulfamic) acid every second day. The 2-3 hours required for this operation does not require shutting down the evaporation stages, as there is sufficient storage capacity in the storage tanks for stripped leachate to keep the evaporator stages operating. When the evaporators are operated discontinuously, scale formation in the heat exchanger tubes becomes more of a problem then when in continous operation; this is especially evident in stage 2.

As scale builds up, the temperature differences between the stages and circulation pump pressure both increase and evaporation rate decreases, as about a third of the tubes clog up. This scale is also quite easily removed by flushing with sulfamic acid twice a week.

RESULTS AND DISCUSSION

Distillate

Analyses of distillate were made every day for 23 days; the results are shown in Table 2. Maximum, minimum, and average values of characteristic components are compared with those guaranteed by the manufacturer of the LCF. Removal of phenols does not meet these guarantees; their concentration in the distillate appears to depend on phenol concentration in the leachate. Chemical oxygen demand (COD) has also often exceeded the guaranteed value. This may be partially due to fractions of the antifoaming agents being carried over in the distillate. Distillate from the leachate of Landfill A often has an organic phase on top of the water layer. This organic layer was never observed during the 2 years pilot study, which was done mainly on leachate from Landfill C, however. Addition of an efficient oil separator has removed this organic layer.

As one would expect, inorganic components are almost completely absent from the distillate. The exception is ammonium, as indicated in Table 2.

Solid residues

LCF produces a solid residue which contains about 1% of water and is of crystalline to pasty consistency depending on pH and the operating mode of the decanter. At pH values below 11.5, the residue appears crystalline; above pH 11.5, a pasty material or a dry, but rather hygroscopic residue is produced according to the way the decanting unit is operated.

Evaporation of the neutralized condensate of the stripper column yields practically pure ammonium sulfate which may be used in appropriate chemical or metallurgical processes. Unexpectedly, the organic content of the residue does not exceed a rather low 1%, eliminating the need for an operation to remove tarry organic residues which was included in the original design.

General performance

With the experience accumulated since May 1986, it can be safely stated that over-all performance of LCF at ZVSMM meets our expectations. Availability is up to a remarkable 75% , a rather satisfactory value for the first months of operating a facility transferred from pilot to full scale for the first time. The energy consumption - about 0.75 t of steam per t of leachate - remains in the range calculated and guaranteed by the equipment supplier. The removal efficiency for the diverse leachate components may be generally considered satisfactory.

Some of the problems presently encountered may well be overcome in the future when the LCF is operated continuously and at full capacity.

FURTHER RESEARCH

There ist immediate need for research on foaming, and possible means to overcome it. Another high priority problem is that of phenolic an other organic compound carry over in the distillate. Some corrosion of pumps has been observed, and this too should be investigated and solved. It was recognized from the beginning that the graphite heat exchangers would be both expensive and hard to maintain. Corrosion samples of four different alternate materials were placed in bypasses in the circulating leachate lines in order to determine if the graphite could be replaced by one of them.

In addition to its contribution to the capital cost of the LCF by the Bavarian state, the Federal German EPA is funding part of the cost of a 2 year research program aimed at optimizing the performance of the process. In addition, these funds will also be used to investigate the possibilities of concentrating aqueous wastes from sources other than landfill leachates in the LCF.

Table 1: Average Concentrations in the Leachates

Parameter	Unit	Landfills A	B	C
conductivity	us/cm	47 480	25 890	72 000
COD	mgO_2/l	10 050	720	3 630
phenol	mg/l	37.5	1.8	19
ammonium	mg/l	934	-	920
chloride	mg/l	8 625	3 760	32 220
sulphate	mg/l	16 759	12 510	59 040
heavy metals	mg/l	43.54	778.75	6.75

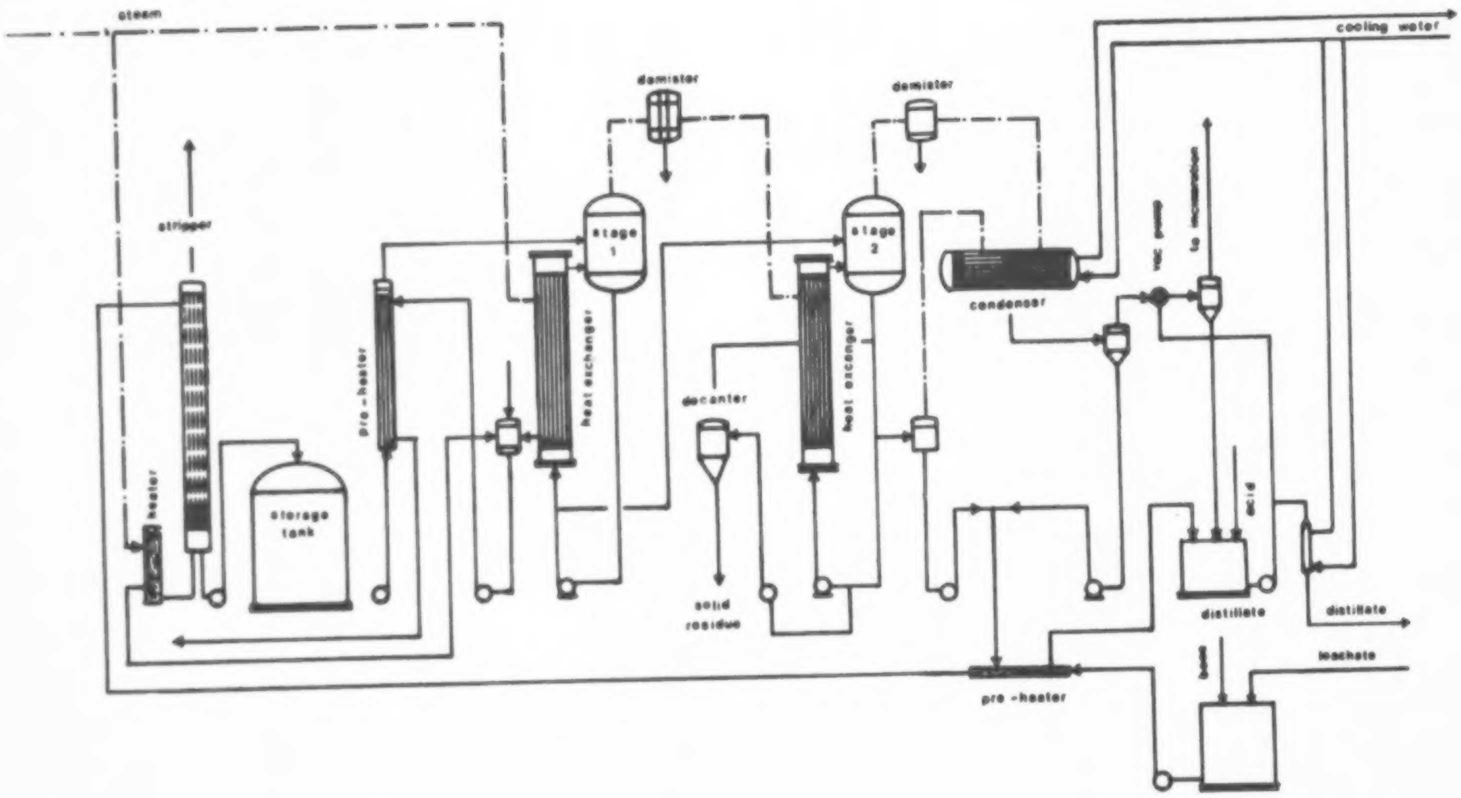
Table 2: Quality of Distillate, Guarantees, Removal Efficiencies

parameter	unit	min.	max.	average	guarant.	removal (%)
conductivity	us/cm	70	400	158	225	99
phenols	mg/l	0.63	27.4	7.68	1.5	76.5
TOC	mgC/l	48.8	168	100.5	135	90
COD	mgO_2/l	227	508	334	300	93
ammonium	mg/l	1.3	282	43.4	70	96

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Figure 1 : flow sheet of LDF


steam
stripper
heater
storage tank
pre-heater
heat exchanger
stage 1
demister
decanter
solid residue
stage 2
heat exchanger
demister
condenser
vac pump
to incineration
cooling water
acid
distillate
distillate
base
leachate
pre-heater

PILOT-SCALE INCINERATION OF A DIOXIN-CONTAINING MATERIAL

Larry R. Waterland, Robert W. Ross, II,
Thomas H. Backhouse, Ralph H. Vocque,
and Johannes W. Lee
Acurex Corporation
Combustion Research Facility
Jefferson, Arkansas 72079

Robert E. Mournighan
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

ABSTRACT

A series of three tests directed at evaluating the incinerability of the toluene stillbottoms waste from trichlorophenol production previously generated by the Vertac Chemical Company were performed in the Combustion Research Facility (CRF) rotary kiln incineration system. This waste contained 37 ppm 2,3,7,8-TCDD as its principal organic hazardous constituent (POHC). Flue gas 2,3,7,8-TCDD levels were less than detectable at all locations sampled. Corresponding incinerator destruction and removal efficiencies (DREs) were greater than 99.9997 percent, based on individual sampling train analyses. By analyzing combined extracts from four simultaneous sampling trains, it was concluded that 2,3,7,8-TCDD DRE was indeed greater than 99.9999 percent. These results suggest that land-based incineration of the Vertac waste is capable of achieving the required DRE and should be considered a treatment option for this waste.

INTRODUCTION

One of the primary functions of the Environmental Protection Agency's (EPA) Combustion Research Facility (CRF) is to perform incineration testing of troublesome hazardous wastes to support decisions regarding whether incineration is a proper waste treatment and disposal option. One class of such wastes is those contaminated with 2,3,7,8-tetra-chlorodibenzo-p-dioxin (2,3,7,8-TCDD or dioxin).

One well-established, highly dioxin-contaminated waste is the toluene stillbottoms from trichlorophenol production previously generated and currently being stored, until a decision regarding appropriate treatment and disposal is reached, at the Vertac Chemical Company in Jacksonville, Arkansas. The generator is currently considering onsite incineration in a mobile incinerator system as an avenue for disposal of this waste and wishes to have a permit for a trial burn issued. The primary objective of the tests reported herein is to evaluate the incinerability of the Vertac toluene stillbottoms waste by determining whether 99.9999 percent DRE could be achieved, as required by current regulations. Results of these incineration tests could, in turn, be used to support any subsequent permit decision.

All tests were performed in the CRF rotary kiln incineration system. The rotary kiln incineration system at the CRF consists of a rotary kiln primary combustion chamber, a fired afterburner, and a primary air pollution control system consisting of a venturi scrubber, wetted elbow, and packed tower scrubber. In addition, a backup air pollution control system (APCS) consisting of a carbon-bed absorber and a HEPA filter is in place. The primary APCS might be considered reflective of what might exist in an actual commercial or industrial incinerator. The backup system is in place to ensure organic pollutant and particulate emissions to the atmosphere are negligible. Results of the tests are summarized in this paper.

PURPOSE

As noted above, the purpose of the tests was to specifically determine whether the stillbottoms waste could be incinerated in a well-operated rotary kiln incinerator, giving 99.9999 percent dioxin DRE, with no contaminated residual streams.

The test program performed consisted of a total of four trial burns. These trial burns consisted of the following:

- A blank burn with the incinerator fired with auxiliary fuel (propane) only to establish background emission levels of pollutants of concern
- A miniburn of short duration (4 hours) with waste fired at nominally 17 kg/hr (38 lb/hr) to demonstrate the ability to feed and incinerate the waste and to gain experience with the sampling protocols specified
- Two full waste test burns of nominally 10-hour duration with the waste fired at about 10 and 18 kg/hr (22 and 39 lb/hr) to specifically address the test objectives

APPROACH

For these tests, waste was introduced at the feed face through the front face lance with a diaphragm-type pump, while auxiliary fuel (propane) was fired through a burner located at the transfer duct end of the kiln. The afterburner was also fired with auxiliary fuel.

For all four tests, propane was fired in the kiln and the afterburner to maintain the kiln at about 1800°F and the afterburner at about 2000°F. For the tests with waste feed, feedrates fluctuated over a wide range, with mean rates of 17 kg/hr (38 lb/hr) for the miniburn; 10 kg/hr (22 lb/hr) for the first full burn; and 18 kg/hr (39 lb/hr) for the second full burn.

System residence times were calculated based on volumetric flowrate measurements using a helium tracer system (2) and the assumption that the kiln and afterburner chamber temperatures were isothermal. The calculated residence time in the kiln main chamber was 5.7 sec for the blank burn, 5.3 sec for the miniburn, and 4.9 and 6.0 sec for the two stillbottoms waste full burns. Residence times in the afterburner were 2.1, 1.9, 1.8, and 2.3 sec for the respective tests.

The generic composition of the toluene stillbottoms waste based on previous data developed by the Vertac Chemical Company (3) and the physical characteristics of the waste based on analysis performed on a sample of the waste at the CRF are given in Table 1. The waste was also analyzed for the organic and trace element priority pollutants. Results of these analyses are given in Table 2. Specific analyses for the Principal Organic Hazardous Constituent (POHC) in the waste, 2,3,7,8-TCDD, showed that it contained 37 ppm of this compound.

Table 1. Stillbottoms waste generic composition (3) and physical characteristics.

Compound	Concentration (percent)
Methanol	1
Toluene	8
Dichlorobenzenes	1.5
Trichlorobenzenes	1.5
2,4,5-trichloroanisole	56
Na-trichlorophenol	7
Dichloromethoxybenzene	16
2,4,5-T, Na salt	7

Parameter	Value (percent)
Bulk density, g/ml	1.37
Loss on drying, percent	13.2
Ash	5.1
Heating value, MJ/kg	16.11
(Btu/lb)	(6945)

Table 2. Composition of the stillbottoms waste.

Component	Concentration[a] (ppm, wt)
Volatile organic priority pollutants	
Methylene chloride	277
Toluene	159,000
All other volatile organic priority pollutants	ND[a]
Semivolatile organic priority pollutants	
1,2-dichlorobenzene	2,690
1,2,4-trichlorobenzene	3,410
All other base/neutral semivolatile priority pollutants	ND[b]
All other acid semivolatile priority pollutants	ND[c]
Trace Elements	
Lead, Pb	4
All other Appendix VIII trace elements	ND[d]

[a] ND denotes not detected at detection limits ranging from 40 to 110 ppm.

[b] ND denotes not detected at a detection limit of 500 ppm.

[c] ND denotes not detected at detection limits ranging from 100 to 500 ppm.

[d] ND denotes not detected at detection limits ranging from 1 to 10 ppm.

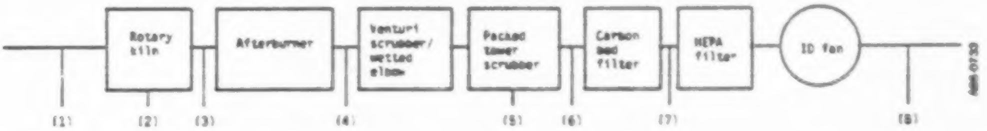
The combustion gas generated during each test was monitored at various locations in the system for CO, CO_2 O_2, NO_x, total hydrocarbon (THC), HCl, particulate, and trace semivolatile organic compounds, most importantly 2,3,7,8-TCDD. In addition, grab samples were obtained of the waste feed, the scrubber system blowdown liquid, and the ash collected in the ash pit during the tests. Ambient air sampling, both in the high-bay incinerator room and in the outside vicinity of the CRF was also performed. Figure 1 summarizes the sampling locations and types of samples obtained.

Waste samples were analyzed for 2,3,7,8-TCDD by dilution, cleanup, and high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS); for the halogenated volatile organic priority pollutants by dilution, purge and trap GC/electron capture detector (ECD) in accordance with Method 8010 (4); for the semivolatile organic priority pollutants by dilution, cleanup, and HRGC/LRMS in accordance with Method 8270 (4); and for the priority pollutant trace elements by acid digestion and atomic absorption techniques (4).

Kiln ash and blowdown water samples were analyzed for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) of chlorine substitution 4 through 8, and for 2,3,7,8-TCDD, by benzene extraction, extract concentration and cleanup, and HRGC/LRMS.

Blowdown water samples were also analyzed for the halogenated volatile organic priority pollutants by purge and trap GC/ECD in accordance with Method 8010 (4); for the semivolatile organic priority pollutants by benzene extraction, extract concentration, and HRGC/LRMS in accordance with Method 8270 (4); and for the priority pollutant trace elements by atomic absorption (4).

Modified Method 5 (MM5) train samples were benzene extracted, extracts for all train components combined, concentrated, and subjected to extract cleanup procedures (1). These extracts were then analyzed for 2,3,7,8-TCDD by HRGC/LRMS. In addition, extracts for the four simultaneous MM5 trains operated downstream of the scrubber system for the two



Sampling point	Description	Grab sample	CO, CO_2 O_2, NO_x	HCl	THC	MM5 for TCDD
1	Waste feed	X				
2	Kiln ash	X				
3	Kiln exit flue gas					X
4	Afterburner exit flue gas		X			X
5	Scrubber blowdown	X				
6	Scrubber discharge flue gas			X	X	X
7	Carbon bed exit flue gas				X	
8	Stack flue gas		X			X

Figure 1. Summary of the general sampling protocol.

full-burn tests were combined and analyzed for 2,3,7,8-TCDD in accordance with Method 8280 (4). The samples from this area of the system, the "virtual stack" are very important since these data will be used to design future systems.

PROBLEMS ENCOUNTERED

Significant problems were experienced with attaining and maintaining waste feed throughout the test program. Specific problems included continued feed lance clogging, due to carbon buildup (coking of the waste material), in the lance, with pump check valve seal failure, and with the ability to pump waste. The feed lance clogging problem was solved by cofeeding water with the waste so that when the lance clogged it would heat and vaporize the water, thereby clearing the clog. Feed line clogging and check valve seal sticking were temporarily solved by cleaning all feed line components with solvent (toluene). However, in retrospect, the choice of a diaphragm pump for this waste was inappropriate. The waste was waxy and very viscous at room temperature. Only at about 95°C (200°F) would it flow sufficiently to be considered pumpable. Hot water heating coils were immersed in the waste for these tests; however, pumping problems persisted. Perhaps a pump of another design, such as a progressive cavity pump, would have provided better service.

RESULTS

Levels of O_2, CO_2, CO, and NO_x in the flue gas at the afterburner exit and in the stack for the four tests performed are summarized in Table 3. As shown, all tests were performed at high excess air; flue gas O_2 was in the 10 to 17 percent range in the afterburner exit and in the 13 to 17 percent range in the stack. CO emissions were always low, <10 ppm, as were NO_x levels, <30 ppm. Table 3 also notes the HCl emission rates for those tests for which these were measured. For the miniburn, the HCl emission rate was 0.45 kg/hr, as measured by the continuous HCl monitor in the scrubber discharge; for the first full burn, the HCl emission rate was 0.25 kg/hr, as measured both by the HCl monitor and by the MM5 trains operated at the scrubber discharge. Both of these are less than the CRF permit level of 0.5 kg/hr.

Particulate levels at both the kiln and afterburner exit were quite low during the background burn with propane fuel alone, as expected. Flue gas particulate levels for the tests with waste feed were highly variable and ranged from several to several hundred mg/dscm. Particulate levels in the scrubber discharge were as high as 340 mg/dscm for one test. Due to technical factors, and since

Table 3. Emission monitor and HCl emission rate data.

Parameters	Background burn 9/4/85	Miniburn 9/9/85	First full burn 9/20/85	Second full burn 9/21/85
Afterburner exit:				
O_2 (percent)	15	12	10	17
CO_2 (percent)	8	7	4	4
CO (ppm)	--[a]	<10	<10	<10
NO_x (ppm)	30	20	10	20
E-duct:				
HCl (kg/hr)				
Continuous Analyzer	--	0.45	0.25	--
MM5 train	--	--	0.25	--
Stack:				
O_2 (percent)	17	18	--	13
CO_2 (percent)	7	3	8	8
CO (ppm)	<10	--	--	--
NO_x (ppm)	--	30	--	--

[a] --denotes monitor not operating or measurement not made.

the O_2 monitor at this location was not operating properly at the time of the test, accurate figures corrected to 7 percent O_2 cannot be derived from the raw data. Since results are uncertain, further work on measurement of particulate emissions from dioxin contaminated waste is needed.

Particulate emissions at the system stack (after the HEPA filter) were also indicated as being much higher than anticipated. The values are 5 to 15 times higher than design values and are, therefore, suspect. Further testing is needed to determine the nature and source of the particulate, if they are indeed as high as indicated.

Table 4 summarizes the 2,3,7,8-TCDD emission levels measured at various locations in the incinerator system for each of the tests. As shown in the table, flue gas levels of 2,3,7,8-TCDD were less than method detection limits at all locations for all tests. These levels correspond to the DRE values noted in Table 4. Two sets of DRE values are noted in the table for the scrubber discharge and stack locations. These correspond to two different measures of flue gas flowrate. One of these was based on a helium tracer injection system; the other was based on the MM5 train velocity measurements. The data in Table 4 suggest that 2,3,7,8-TCDD DRE was generally greater than 99.9997 percent in the scrubber discharge, which would likely correspond to the stack of an actual hazardous waste incinerator.

Method detection limits were not low enough to establish that greater than 99.9999 percent DRE was achieved either in the scrubber discharge or at the system stack. Therefore, the extracts from the four MM5 trains operated at the scrubber discharge for the two full-burn tests were combined and reanalyzed in an attempt to achieve better detection limits. Calculated 2,3,7,8-TCDD levels and corresponding 2,3,7,8-TCDD DREs, based on the combined extract analyses for the second full burn are given in Table 5. The data for the second full burn clearly show that greater than 99.9999 percent DRE was achieved. The extracts for the first full burn were spiked with an order-of-magnitude higher level of recovery standard than appropriate by the off-site laboratory which originally analyzed the individual train extracts. As a consequence, method detection limits corresponding to ng/dscm of flue gas were not better than for the individual train analysis data, as summarized in Table 4.

The kiln ash and the scrubber blowdown water from this entire test series was analyzed for PCDDs and PCDF of chlorine substitution 4 through 8. The kiln ash samples were generally devoid of PCDDs and PCDF to detection limits ranging from 3 to 40 ppt. Similarly, the scrubber blowdown samples were devoid of all PCDDs and PCDFs; except octa-CDDs which were present at 0.07 ppt. This is not surprising since octa-CDDs are relatively common in environmental samples, and the level measured was quite low.

The scrubber blowdown was also analyzed for the organic and trace element priority pollutants. No organic priority pollutant was present in the blowdown at levels greater than 10 ppb. In addition, none of the trace elements was present at concentrations which would cause the blowdown water to be considered EP (Extraction Procedure) toxic. Based on all analytical data, the blowdown would not be considered a hazardous waste.

Table 4. 2,3,7,8-TCDD emissions and DRE

Date and test location		2,3,7,8-TCDD emissions (ng/dscm)	2,3,7,8-TCDD DRE (percent)	
			Based on helium tracer	Based on flue gas velocity
Miniburn				
Kiln exit:	Train 1	<0.74	>99.99995	
	Train 2	<1.4	>99.99991	
Afterburner exit:	Train 1	<13	>99.9984	
	Train 2	<11	>99.9986	
First Full Burn				
Kiln exit:	Train 1	<0.55	>99.99992	
	Train 2	<0.17	>99.99998	
	Average			
Afterburner exit:	Train 1	<3.8	>99.99903	
	Train 2	<1.3	>99.99967	
Scrubber system discharge:	Top train	<0.43	>99.99982	>99.99987
	Bottom train	<0.51	>99.99979	>99.99985
	Left train	<2.5	>99.99896	>99.99925
	Right train	<0.55	>99.99977	>99.99983
	Average			
Stack:	East train	<2.3	>99.99907	>99.99916
	South train	<1.5	>99.99945	>99.99951
	Average			
Second Full Burn				
Kiln exit:	Train 1	<6.4	>99.99964	
	Train 2	<21	>99.99988	
Afterburner exit:	Train 1	<3.9	>99.99956	
	Train 2	<2.8	>99.99969	
	Average			
Scrubber system discharge:	Top Train	<1.9	>99.99969	>99.99974
	Bottom train	<2.0	>99.99967	>99.99973
	Left train	<2.2	>99.99864	>99.99970
	Right train	<0.76	>99.99988	>99.999897
Stack:	East train	<1.5	>99.99975	>99.99974
	South train	<1.6	>99.99973	>99.99973
	Average			

Table 5. 2,3,7,8-TCDD emissions and DRE based on combined scrubber discharge train extracts

Test date	2,3,7,8-TCDD emissions (ng/dscm)	2,3,7,8-TCDD DRE	
		Based on helium tracer	Based on flue gas velocity
Full burn 9/21/86	<0.066	>99.999989	>99.999991

In summary, a series of incineration experiments was performed with the Vertac Chemical Company's toluene stillbottoms waste from trichlorophenol production. This waste is one of the more well known of the dioxin-contaminated wastes presently in existence. Samples of the waste tested in this study contained an average of 37 ppm 2,3,7,8-TCDD (37 μg/g). Three incineration tests were performed in the CRF rotary kiln incineration system with a nominal waste feedrate of 20 kg/hr.

With regard to the principal objectives of these tests, the following can be concluded:

- 2,3,7,8-TCDD DRE, based on the combined extracts from the four MM5 trains in the scrubber discharge, was greater than 99.9999 percent for one test. For the other test, method detection limits prevented quantitating that better than 99.9998 percent DRE was achieved.
- Accurate determination of particulate emissions at the virtual stack and system stack was not achieved. Further research is needed to obtain data on the amount, nature, and source of particulate emissions from these sources.
- HCl emissions in the virtual stack ranged from 0.2 to 0.45 kg/hr. These results are less than both the RCRA standard of 1.8 kg/hr, and the CRF permit limit of 0.5 kg/hr.
- Scrubber blowdown has characteristics which allow it to be delisted as a hazardous waste.

The conclusions suggest that incineration should be considered a viable treatment method for this stillbottoms waste, given that appropriate safeguards are employed. The data in this study confirm that an incinerator, operating under proper conditions, can achieve greater than 99.9999 percent DRE for 2,3,7,8-TCDD, with HCl emissions below the regulatory limit.

ACKNOWLEDGEMENTS

The work reported in this paper was supported by EPA's Hazardous Waste Environmental Research Laboratory under EPA Contracts 68-03-3128 and 68-03-3267. The guidance and support of the former EPA Project Officer, Richard A. Carnes, is gratefully acknowledged.

REFERENCES

1. American Society of Mechanical Engineers, 1984, Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs), ASME Environmental Standards Workshop, September 18.

2. Carnes, R. A. and F. C. Whitmore, 1984, Characterization of the Rotary Kiln Incineration System at the USEPA Combustion Research Facility (CRF), Hazardous Waste, Vol. 1, No. 2, p 225.

3. Federal Register, Vol. 51, No. 106, June 3, 1986, pp 19850-19863.

4. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, 2nd ed., July 1982.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

SUPERCRITICAL FLUID EXTRACTION AND CATALYTIC OXIDATION OF TOXIC ORGANICS FROM SOILS

Kerry M. Dooley[1], Robert Gambrell[2] and F. Carl Knopf[1]**

Department of Chemical Engineering[1]
Department of Marine Science[2]
Louisiana State University
Baton Rouge, Louisiana 70803

ABSTRACT

Supercritical fluid (SCF) extraction is a promising new technique for the cleanup of soils, sediments, and sludges that are contaminated with hazardous wastes. In this investigation, supercritical carbon dioxide (SC-CO_2) has been used to extract PCBs, DDT, and toxaphene from contaminated topsoils and subsoils. An attractive feature of this process is that the CO_2, being virtually inert, leaves no solvent residue on the processed soil.

In our initial extraction studies, supercritical CO_2 at 100 atm and 40°C was continuously passed through a fixed bed of 10 g of soil. Approximately 70% of the DDT and 75% of the toxaphene could be leached from a topsoil (12.6% organic matter) contaminated with 1000 ppm DDT and 400 ppm toxaphene in under ten minutes using SC-CO_2 at a rate of 0.7 g/s. The extraction of contaminated (with 1000 ppm Aroclor 1254) subsoil (0.74% organic matter) proved to be even more promising, because more than 90% of the PCBs could be extracted in under one minute at the same CO_2 rate.

Recently SC-CO_2 with a single entrainer*, either methanol or toluene, was compared to pure CO_2; comparison was made on the basis of extraction rate and the removal efficiency for DDT or PCBs from contaminated topsoils. The supercritical mixtures at 100 atm and 40°C were continuously passed through a fixed bed of 10 g of soil. The most effective solvent system, SC-CO_2 with 5 wt% methanol at a flowrate of 0.7 g/s, was able to leach 95% of the DDT from the soil in under 5 minutes, as compared to either pure CO_2 or CO_2 with 5 wt% toluene at the same conditions, which resulted in only 70% extraction in 10 minutes. This same extraction mixture (SC-CO_2 with 5 wt% methanol) was also applied to a highly contaminated spill site topsoil containing ca. 3500 ppm Aroclor 1260 and 2100 ppm Aroclor 1242. Over 98% extraction of the contaminants was realized in 10 minutes.

With the demonstrated ability to extract contaminants from soils using supercritical CO_2 with an entrainer, a logical further treatment would be the destruction of the wastes while they are in the supercritical phase. An evaluation of catalysts for the low temperature (below 350°C) oxidation of polycyclic aromatic hydrocarbons and chlorinated hydrocarbon wastes in the SCF phase will be presented.

---

[*] An entrainer is a volatile organic compound which, when added in low levels to supercritical CO_2, dramatically increases the solubilities of certain nonvolatile organics in the SCF.

[**] To whom correspondence should be addressed.

INTRODUCTION

Supercritical fluid (SCF) extraction has received much attention as a technique for separating relatively nonvolatile materials (Paulaitis et al., 1982). Typically in SCF extraction a solvent gas such as carbon dioxide, at high pressure and moderate temperature, is contacted with a solid or liquid phase. Slight changes in the system temperature or pressure can cause large changes in the solvent density and consequently in its ability to solubilize relatively nonvolatile components. For example, at 200 atm and 35°C the density of CO_2 approaches 0.8 g/cc and at these conditions a solute such as naphthalene would have a solubility some 10,000 times that predicted if CO_2 behaved as an ideal gas. By taking advantage of these facts a process can be envisioned whereby manipulation of the system pressure effects extraction of a nonvolatile material. A pressure letdown, to a pressure below the system critical conditions, can cause near complete precipitation of the relatively nonvolatile material from the solvent. In addition to the liquid-like densities of a typical SCF, viscosities and molecular diffusivities of SCFs are intermediate to typical liquid and gas values for these properties. For these reasons the extraction efficiencies of SCFs are usually higher than those of liquids.

The many advantageous properties of SCFs have opened up new technologies in environmental control; the subject has been recently reviewed by Groves, Brady and Knopf (1985). Successful efforts have included the use of SCFs in: the regeneration of adsorbents contaminated with volatile organics using pure SC-CO_2 (Eppig et al., 1981); oxidation of organic contaminants in waste streams using SC-water (Modell, 1982); liquid-liquid extraction of waste streams again using pure CO_2 as the extraction medium (Ringhand and Kopfler, 1983); the extraction/reaction comprising the generation of low sulfur chars from coals utilizing either SC-toluene or SC-alcohols (Vasilakos et al., 1985); and finally the regeneration with SC-CO_2 of activated carbon used in the cleanup of liquid waste streams (de Filippi et al., 1980a). The regeneration of activated carbon was not universally practical, because the buildup of irreversibly bound organics frustrated some applications.

We are currently examining the capabilities of supercritical fluids to extract toxic chemicals such as DDT and PCBs from soils, thereby providing a tool for cleaning up hazardous waste sites. Such removal offers the obvious advantage of the creation of a much smaller volume if further treatment such as combustion, biological degradation or other disposal method is desired.

In conventional extraction technology the pressure would be reduced subsequent to extraction, precipitating a solid or liquid phase rich in organic contaminants from the CO_2. In order to recycle the CO_2, the contaminant level in the CO_2 must often be further reduced by distillation (deFilippi et al, 1980b). In addition, since the pressure of the CO_2 has been substantially lowered, recompression is necessary.

In conjunction with our work with SC-CO_2 plus entrainers, we are investigating an alternative to the above separation scheme. We are attempting to totally oxidize the extracted organic contaminants by passing the high pressure mixture plus air over total oxidation catalysts such as CuO. Temperatures necessary for total oxidation should be in the 420-600 K range, this being characteristic of free-radical assisted autoxidation processes (Schuit and Gates, 1980). After drying to remove the water formed in the reactions, and neutralization, both of which can be accomplished at high pressure, the CO_2 can be recycled with small recompression costs.

In order to explain the extraction process, the thermodynamics involved, and oxidation catalysis in a supercritical fluid medium, this paper is divided into two sections. The first discusses background, including early SCF extraction results and the phase equilibria expected for the ternary system of CO_2-methanol-DDT (here methanol is an entrainer), and briefly introduces both reactions in SCFs and catalytic autoxidation of priority pollutants. The second section presents recent data on the effectiveness of CO_2 with entrainers for the extraction of DDT and PCBs from topsoils of high organic content. Some preliminary data showing the solid-catalyzed partial oxidation of a pollutant (toluene) in a SCF are also presented.

PAST RESULTS

In previous work (Brady et al., 1987) we investigated the use of pure SC-CO_2 to extract PCB's, DDT and toxaphene from a contaminated topsoil (12.6% organic matter) and subsoil (0.74% organic matter). Experiments with SC-CO_2 continuously flowing through a fixed bed of 10 grams of contaminated soils showed that over 90% of the PCBs (original contamination level 1000 ppm) could be extracted from the subsoil in under one minute using a CO_2 flowrate of 0.7 g/s. However, only 70% of the DDT and 75% of the toxaphene could be leached from the topsoil contaminated with 1000 ppm DDT and 400 ppm toxaphene in 10 minutes at the same CO_2 rate. These results are not unexpected in that pure SC-CO_2, being a relatively nonpolar solvent, would show only non-specific van der Waals interactions with adsorbed compounds that may be strongly bound to polar sites on the topsoil. The presence of these sites is consistent with the high organic content of the topsoil. Mixed solvents, for example CO_2 and a few wt% of a polar entrainer, could result in specific chemical attraction of adsorbate and extraction medium, and thus enhance contaminant extraction from solids containing polar adsorption sites, such as activated carbon or topsoils of high organic content.

PHASE DIAGRAMS

The "entrainer" solvents used in this work to date are toluene and methanol. By using the Peng-Robinson cubic equation of state (Peng and Robinson, 1976), the triangular phase diagram for the ternary system CO_2-DDT-methanol at 40°C, 100 atm can be constructed as shown in Figure 1.

It is assumed the solubility of the solvent (CO_2 with methanol) in solid DDT (component 2) is negligible. The solid phase is considered pure DDT, and its fugacity f_2^{os} in phase equilibria calculations was evaluated from

$$\ln \frac{f_2^{os}}{f_2^{ol}} = \frac{\Delta H^f}{k} \left(\frac{1}{T_{m_2}} - \frac{1}{T} \right) - \int_0^P \frac{V_2^{ol} - V_2^{os}}{RT} \, dP \quad . \qquad (1)$$

assuming the Peng-Robinson equation is valid for calculating the fugacity of the pure subcooled liquid (f_2^{ol}). The critical points are calculated according to the algorithm proposed by Heideman and Khalil (1980).

At 40°C and 100 atm, the addition of a small amount of toluene or methanol to CO_2 increases the DDT solubility. The solubility of DDT in a mixed solvent of 95 wt% CO_2 and 5 wt% toluene is estimated as 2.5×10^{-3} (~3.6 times the value in pure CO_2). If toluene is replaced by methanol the estimated DDT solubility from Figure 1 is 0.01 (~14 times that in pure CO_2). Therefore a mixed solvent with 95 wt% CO_2 and 5 wt% methanol should be more effective in extracting DDT from soil than a mixed solvent with 95 wt% CO_2 and 5 wt% toluene, although the latter is still a more effective solvent than pure CO_2. The approximate supercritical phase compositions for the ternary system at the operating conditions are summarized in Table I. The interaction parameter k_{ij} (k_{ij} = 0.07) was empirically determined by regressing VLE data for the binary system of CO_2 plus methanol (Semenova et al., 1979). The phases present ("conditions") are denoted by either SFE (solid and SCF at equilibrium) or SLVE (solid-liquid-vapor phases at equilibrium).

Table I. Compositions of Supercritical Fluid Phases for CO_2-Entrainer-DDT-Systems

System	k_{ij}	Mol Fraction (40°C, 100 atm)		Condition
$CO_2(1)$ + DDT(2)	0.07	$y_2 = 0.7 \times 10^{-3}$		SFE
DDT(2) + Methanol	0	$y_2 = 0.3 \times 10^{-3}$		SFE
CO_2 + DDT + Methanol		$x_2 = 0.055$	$x_3 = 0.132$	SLVE
		$y_2 = 0.014$	$y_3 = 0.079$	
		$x_2 = 0.032$	$x_3 = 0.115$	critical pt

REACTIONS IN SUPERCRITICAL SOLVENTS

Supercritical fluids have potential advantages as solvents in coal liquefaction, high temperature thermal condensations and alkylations, catalyzed hydrocarbon isomerizations, and oxidation reactions. The application of SCF solvents improves the final product distributions of these reactions, sometimes by diminishing heat and mass transport limitations, and sometimes by allowing separation of desired products prior to further reaction in a solid or liquid phase. Currently, the most promising application of SCF as reaction media is coal liquefaction/extraction, where the condensed extract is a fuel or chemical feedstock comparable to hydrogen-intensive processes. These findings have prompted a growing interest in reactions using supercritical fluid media, the subject has been recently reviewed (Subramaniam and McHugh, 1986).

The utility of SCF as reaction media, apart from their utility in coal processing, is documented. SCF have proven feasible as reaction media for high temperature deep oxidations (Modell, 1982), where SC water homogenizes heavy organic-air-salt mixtures and thereby enhances combustion efficiencies.

SCF have also proven feasible as reaction media for hydrocarbon isomerization processes, either with a homogeneous or heterogeneous catalyst (Kramer and Leder, 1975, Tiltscher et al., 1981). The details of the isomerization processes are sketchy but interesting. In the homogeneous process, the SC paraffin reactant solubilizes not only the most efficient catalyst, $AlBr_3$, but also H_2, which controls the selectivity of this reaction by suppressing cracking rates. Isomerization-to-cracking ratios of better than 50 were obtained at optimum reaction conditions.

Finally, Metzger et al. (1983) have found that many compounds containing carbonyls or double bonds will undergo condensation and alkylation reactions at temperatures not much above their critical temperatures, in the 300-600K range. At these conditions they prepared, for example, the cyclohexane addition products to acrylonitrile, heptene-1, and methyl acrylate in high yields. The intermediates in these reactions were remarkable stable with respect to polymerization.

In summary, it has been observed that SCF provide favorable reaction media in the following cases:

(1) Where homogenization of the reaction mixture removes diffusion limitations for a key reactant, catalyst, or promoter;

(2) Where the SCF separate unstable products of reaction from a solid or liquid phase.

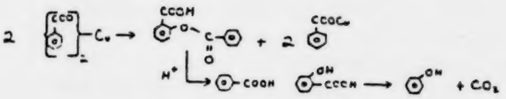
(3) Where the SCF play a direct role in reaction, say, in the stabilization of free radicals or other intermediates, or assisting in the transfer of hydrogen.

(4) Where the SCF aid in the solubilization of reaction products that could result in catalyst deactivation.

TOTAL CATALYTIC OXIDATION OF PRIORITY POLLUTANTS

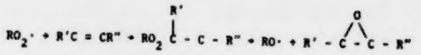
The chemical behavior with respect to catalytic total oxidation of the many compounds listed as priority pollutants (U.S. EPA, 1980b; Robertson et al., 1980) is so diverse that not all compound classes could be studied. This is true even if we restrict ourselves to single model compounds or well-characterized mixtures of homologous compounds. Our attention has been focused on three classes of difficult-to-oxidize compounds: (1) Single-ring aromatics with deactivating side groups, such as chlorobenzenes, chlorobenzidines, and nitrophenols; (2) Fused-ring polycyclic aromatic hydrocarbons (PAHs) such as anthracene and benzanthrene; (3) Chlorinated biphenyls and naphthenic compounds such as DDT, PCBs, and dieldrin. Our catalytic oxidation work is not performed independently of the entrainer studies; feeds to be oxidized include the entrainer, which in some cases will be oxidized as well. Entrainer oxidation is often desirable, since in free radical processes small molecules that can form radicals easily (acetone, for example) help initiate the more difficult free radical oxidations of the refractory compounds. Such oxidizable initiators are known as co-oxidants and represent a more economical solution to the initiation problem than do such common initiators as peroxides.

We have examined total oxidation by free-radical-assisted redox processes, which are well known for the partial oxidations of alkylaromatic and naphthenic hydrocarbons in aqueous or organic solutions; the reaction mechanisms and applicable catalysts are exhaustively surveyed by Kaeding et al. (1970), Sheldon and Kochi (1974), Schuit and Gates (1980), and Parshall (1980). The catalysts are organometallic redox couples containing, for example, Co^{2+}/Co^{3+}. Peroxides and hydroperoxides are the primary products, which decompose to more stable products at temperatures above about 80-100°C. Typical pathways for a typical reaction, the oxidation of toluene to benzaldehyde/benzoic acid, are given in Fig. 2. In the presence of acids, condensation takes place concurrently with oxidation, resulting in the production of phenols and acetates. A typical pathway for toluene oxidation is given below:



The processes and catalysts common to solution can be adapted to a dense gas (supercritical) phase and certain solid heterogeneous catalysts. We have demonstrated this in a recently completed study of the oxidation of toluene to benzaldehyde with feeds composed mostly of supercritical CO_2 and some air (Dooley and Knopf, 1986). Not all redox-containing catalysts are effective; in fact, in catalytic reaction experiments employing a series of Co and Co-Mo oxides supported on Al_2O_3, only one catalyst with a specific Co^{2+}/Co^{3+} initial ratio was both active for partial oxidation and inactive for the undesired condensation reactions to polycyclic products. For this work the temperatures were in the 180-220°C range and the catalysts were not modified with electron transfer promoters (as they are in solution) to enhance their activities.

At slightly higher temperatures and with the inclusion of electron transfer promoters in the solid catalyst, peroxides and hydrogen peroxides are more easily produced and then ruptured at the O-O bond. The rupture results in a net increase in the number of free radicals and therefore in a dramatic increase in oxidation rates. Schuit and Gates (1980) have shown that at these conditions the total concentration of peroxides and hydroperoxides is proportional to the exponential of the product of the rate of formation of all products times the reactor residence time. Therefore once initiated this process must result in complete oxidation of all oxidizable species present in the feed, if the amount of catalyst employed is large enough. One way in which olefinic, aromatic, and other double-bond containing molecules can be totally oxidized is through free-radical epoxidation on a surface or even by desorbed radicals in the fluid-phase (Haber, 1985):



$$RO_2\cdot + R'C = CR'' + RO_2\overset{R'}{\overset{|}{C}} - C - R'' + RO\cdot + R' - \overset{O}{C - C} - R''$$

The reason why total oxidation is not more prevalent in solution is that the reaction conditions are carefully chosen to inhibit this generally undesired reaction: the solutions are O_2 starved due to the low solubilities of low-pressure air in most organics, and the solutions often contain polar compounds (acetic acid, for example) which act as free radical traps. Both of these limits on total oxidation will be removed in the proposed process. The upper limit on free-radical-assisted total oxidation is about 300-350°C; above these temperatures the reverse rates of hydroperoxide formation reactions are large enough that oxidation must take place by other routes.

Simple oxides may not catalyze the total oxidation of refractory aromatic and naphthenic compounds. The ideal catalyst must be able to adsorb the hydrocarbon by electron transfer to or from a metal cation site, to insert electrophilic oxygen to form aldehydes or epoxides, and finally to decompose these to carbon oxides.

EXPERIMENTAL METHODS FOR SCF SOIL EXTRACTIONS

Two contaminated topsoils were obtained for our extraction experiments. The first topsoil was obtained from a DDT spill site near Lake Providence, Louisiana. The second topsoil was obtained from a PCB spill site. The soils were air-dried (35°C) and the initial DDT or PCB levels checked via EPA-approved test procedures (U.S. EPA, 1980; 1982).

A schematic diagram of the SC-CO_2 extraction apparatus is given in Figure 3. Liquid CO_2 at ambient temperature is fed to a diaphragm compressor and compressed to a pressure between 200 and 350 atm. The compressed CO_2 is stored in surge tanks to dampen any pressure fluctuations. From the surge tanks the CO_2 flows at ~0.7 g/s to a vertical tube fixed bed containing the contaminated soil; the pressure here is controlled to ±5 psi. Upstream of the vertical tube, approximately 5 wt% of either toluene or methanol are combined with the supercritical CO_2 by the use of a Ruska high-pressure metering pump. In the tube the fixed bed of contaminated soil is contacted by the mixed solvent. The extraction pressure is monitored by a Heise digital pressure gauge. Both the feed line and the fixed bed are immersed in a constant temperature bath maintained at 40 ± 1°C. Downstream of the bed two micrometering valves are used to control the solvent flow rate and reduce the pressure to atmospheric. The extract mixture is first passed through two dry ice/acetone cold traps to collect the precipitated contaminants, followed by an activated carbon trap, and finally by a dry test meter to totalize the solute-free CO_2. All wetted parts of the apparatus are stainless steel, teflon, or viton.

The residual concentration of DDT or PCBs in the soil is measured according to EPA-approved test procedures (U.S. EPA, 1980; 1982). Typically 5 g of soil are weighed to ± 0.01 g into cellulose extraction thimbles, which are placed in a Soxhlet apparatus and extracted for 8 hours with a 60/40 mixture of acetone/hexane. The acetone/hexane extracts are then washed with water to remove acetone, and the hexane portion is subjected to florisil cleanup and finally diluted with hexane as necessary for analysis by gas chromatography.

SCF EXTRACTION OF DDT CONTAMINANTED TOPSOIL - RESULTS AND DISCUSSION

The initial DDT level of the contaminated topsoil was 1271 mg/kg. Extractions of this test soil showed that approximately 60-70% of the DDT could be removed in approximately 10-20 minutes as shown in Figure 4. Longer-time extractions using pure SC-CO_2 did not show any improvement over this reduction. These data imply that a portion of the DDT is strongly bound to the soil and that SC-CO_2 at these conditions cannot extract this strongly-bound DDT.

Using the same extraction conditions as with pure SC-CO_2 (40°C, 100 atm, flow rate ~ 315 cm^3/s at 25°C, 1 atm), the two mixed solvent systems (CO_2-toluene and CO_2-methanol) were investigated. These data are plotted in Figure 4 along with the extraction data obtained using pure SC-CO_2 solvent. Little if any improvement in extraction efficiency is observed upon comparing the data for SC-CO_2 with 5 wt% toluene to that for pure SC-CO_2. A maximum of 60-70% of the DDT can be removed in 10-20 minutes with either solvent system. Extraction with SC-CO_2 and 5 wt% methanol, however, is more successful. Approximately 95% of the contaminants can be removed in 5 minutes or less (Figure 4). These results imply that for maximum extraction efficiency a mixed solvent system should be used, where the entrainer or co-solvent is tailored to the soil type and the solute being extracted.

To determine the rate-limiting-step of the extraction process, we also carried out extractions of DDT-contaminated topsoils at various SC-CO_2 flowrates, while maintaining the methanol entrainer composition at 5 wt%. These results are presented in Table II. The data indicate that the process is apparently not external-transfer limited (in the fluid phase).

Table II. Variation of Soil Concentration in the Extraction of DDT-Contaminated, Spill-Site Topsoil using SC-CO_2 with 5 wt% Methanol

Conditions: 40°C, 100 atm, 470 and 47 cm^3/sec

Extraction Time (min)	470 cm^3/sec @ 25°C, 1 atm	47 cm^3/sec @ 25°C, atm
0	1271	1271
1	221, 207*	—
1	222, 236	—
2	82, 105	—
2	95, 94	—
5	66, 58	60
5	58, 61	—
10	52, 37	—
10	59, 48	—
20	—	86
40	—	36
60	—	51
120	—	25

*Multiple entries in concentration column are replicate analyses.

SCF EXTRACTION OF PCB CONTAMINATED TOPSOIL - RESULTS AND DISCUSSION

To again demonstrate the effectiveness of SC-CO_2 with 5 wt% methanol, this solvent system was used to extract a spill site topsoil containing ca. 3,500 ppm Aroclor 1260 and 2,100 ppm Aroclor 1242. The results, plotted in Figure 5, show over 98% removal of the contaminant is possible within a 10 minute extraction period.

EXPERIMENTAL METHODS FOR SCF OXIDATION STUDIES

We are currently investigating the oxidation of toluene with redox catalysts, using the system shown in Fig. 6. CO_2 is compressed to slightly above critical conditions (T_c = 31°C and P_c = 72.8 atm), and at a flow rate of 1 g/s is mixed with toluene delivered by a metering pump and air from a cylinder. All flow rates are controlled by metering valves. The reaction mixture is ca. 1.5 wt% toluene, 1.5% oxygen, 5% N_2, and 92% CO_2, and is controlled at 30-300°C ±1°C by encasing the reactor (½" o.d. tube with a fritted disk) in an insulated heat source (4" o.d. heated alumnium block). For the initial experiments the pressure at the reactor was 80 atm although the reactor is capable of pressures in excess of 300 atm.

Before the reactor, the air/CO_2 ratio and toluene/CO_2 ratio are checked by on-line sample injection into a gas chromatograph with a thermal conductivity detector; after the reactor, product samples are injected into an on-line gas chromatograph interfaced to a mass spectrometer (Extrel Model ELQ 400) for detailed analysis. The products are then cooled by expansion through a heated micro-metering valve. The uncondensed CO_2 is passed through a totalizing meter.

It was possible to dissolve 1.5 wt% toluene and 6.5 wt% air in supercritical CO_2 at 80 atm and 293-493K. Using this mixture the toluene could be oxidized at low rates and conversions to benzaldehyde, benzyl alcohol, the cresol isomers, and a lesser amount of condensation products and carbon oxides. A 5% CoO/Al_2O_3 catalyst, calcined at 200°C in order to preclude oxidation to Co_3O_4 and the cobalt "aluminates", proved to be an active and selective (for partial oxidation) catalyst. Its turnover number for partial oxidation was about 10^{-5}/s at 473K.

SUMMARY

We have reported the use of SC-CO_2, with either toluene or methanol as an entrainer, for the extraction of DDT and PCBs from contaminated topsoils. The extraction efficiency was shown to be a strong function of the entrainer selected. A supercritical mixture of CO_2 plus 5 wt% toluene showed no improvement over CO_2 alone, with only ~ 75% removal of the DDT possible; the residual DDT was strongly adsorbed on the soil. However, near complete removal of DDT was possible using SC-CO_2 with 5 wt% methanol at 40°C and a flowrate of 0.7 g/s. The efficiency of the CO_2-methanol system remained unchanged with a large variation in flowrate, from 1 g/s to 0.1 g/s, demonstrating that no external transfer resistances are present at these conditions. Near complete removal of a mixture of Aroclor 1260 and Aroclor 1242 was also possible using SC-CO_2 with 5 wt% methanol at 40°C and a flowrate of 0.7 g/s. Once these contaminants have been dissolved in the SCF phase, partial oxidation is feasible if catalyzed by certain supported metal oxides. Further work on total oxidation by supported mixed-metal oxides is in progress.

ACKNOWLEDGMENT

This study was supported in part by Grant CR-809714 from the US Environmental Protection Agency. This support does not signify that the contents necessarily reflect the views and policy of the Agency; no mention of trade names or commerical products constitute endorsement or recommendation for use. We acknowledge the experimental assistant of DeAnn Leach and James Torres.

NOMENCLATURE

F = fluid phase

f = fugacity, atm

ΔH^f = heat of fusion, cal/mol

k = interaction parameter

L = liquid phase

P = pressure, atm

R = gas constant, 1.987 cal/mol-°K or 82.06 atm-cm^3/mol-°K or soil particle radius, cm

S = solid phase

T = temperature, °K

V = vapor phase or molar volume, cm^3/mol

SUBSCRIPTS

m = melting point

o = initial value

1 = supercritical solvent

2 = solute

SUPERSCRIPT

$o\ell$ = pure subcooled liquid

os = pure solid

REFERENCES

Brady, B.O., Kao, C.-P., Gambrell, R.P., Dooley, K.M., and Knopf, F.C., Ind. Eng. Chem. Research, 26, 261 (1987).

deFilippi, R.P., Krukonis, V.J., Robey, R.J., and Modell, M., EPA Report - 600/2-80-054, National Technical Information Service, Washington, D.C., 1980a.

deFilippi, R.P., Krukonis, V.J., Robey, R.J., and Modell, M., United States EPA Report No. 600/2-80-054; EPA Office of Research and Development: Research Triangle Park, North Carolina, 1980b.

Dooley, K.M., and Knopf, F.C., 1986, submitted to Ind. Eng. Chem. Research.

Eppig, C.P., deFilippi, R.P., and Murphy, R.A. United States EPA Report No. 600/2-82-067; EPA Office of Research and Development: Research Triangle Park, North Carolina, 1981.

Gates, B.C., Katzer, J.R., and Schuit, G.C.A., Ch. 4 of "Chemistry of Catalytic Processes," McGraw-Hill, 1979.

Groves, F.R., Brady, B.O., and Knopf, F.C., CRC Reviews in Env. Control 15, 237 (1985).

Haber, J., ACS Symp. Ser. 279, 3 (1985).

Heideman, R.A., Khalil, A.M., AIChE J 26, 769 (1980).

Kaeding, W.W., Lindblom, R.O., Temple, R.G., and Mahon, H.I., Ind. Eng. Chem. Proc. Des. Dev. 4, 97 (1965).

Kramer, G.M. and Leder, F., U.S. Patent 3,880,945 (1975).

Metzger, J.O., Hartmanns, J., Malwitz, D., and Koll, P. in "Chemical Engineering at Supercritical Fluid Conditions," Paulaitis, M.E., Penninger, J.M., Gray, R.D., and Davidson, P. (eds.), p. 515 (1983).

Modell, M., Gaudet, G.G., Simson, M., Hong, G.T., and Biemann, K., Eighth Annual Research Symp. Land Disposal, Incineration and Treatment of Hazardous Waste, Ft. Mitchell, March 8 to 10, 1982.

Parshall, G.W., Chs. 7 and 10 of "Homogeneous Catalysis," Wiley, 1980.

Paulaitis, M.E., Krukonis, V.J., Kurnik, R.T., and Reid, R.C., Rev. Chem. Eng. 1, 1791 (1982).

Peng, D.Y; Robinson, D.B., Ind. Eng. Chem. Fundam. 15, 59 (1976).

Ringhand, P.H. and Kopfler, F.C., 186th National Meeting of the American Chemical Society, Washington, D.C., August 28 to September 3, 1983.

Robertson, J.H., Cowen, W.F., and Longfield, J.Y., Chem. Eng., June 30, 1980, p. 102.

Schuit, G.C.A. and Gates, B.C., pp. 461-475 of "Chemistry and Chemical

Engineering of Catalytic Processes," R. Prins and G.C.A. Schuit, Eds., Sijthoff and Nordhoff, 1980.

Semenova, A.I., Emel'yanova, E.A., Tsimmerman, S.S., and Tsiklis, D.S., Russ. J. Phys. Chem. 53, 1428 (1979).

Sheldon, R.A. and Kochi, J.K., Adv. Catal. 25, 272 (1974).

Subramaniam, B. and McHugh, M.A., Ind. Eng. Chem. Proc. Des. Dev. 25, 1 (1986).

Tiltscher, H., Wolf, H., and Schelschorn, J., Angew. Chem. Int. Ed. Engl. 20, 892 (1981).

U.S. EPA; "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue"; U.S. EPA, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio, 1980.

U.S. EPA, "Priority Pollutant Frequency Listing Tabulations and Descriptive Statistics", U.S. EPA, Effluent Guidelines Division, 1980b.

U.S. EPA 600/4-82-057; "Organochlorine Presticides and PCB's-Method 608"; U.S. EPA Environmental Montioring and Support Laboratory: Cincinnati, Ohio, 1982.

Vasilakos, N.P., Dobbs, J.M., and Parisi, A.S. Ind. Eng. Chem. Process Des. Dev. 24, 121 (1985).

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

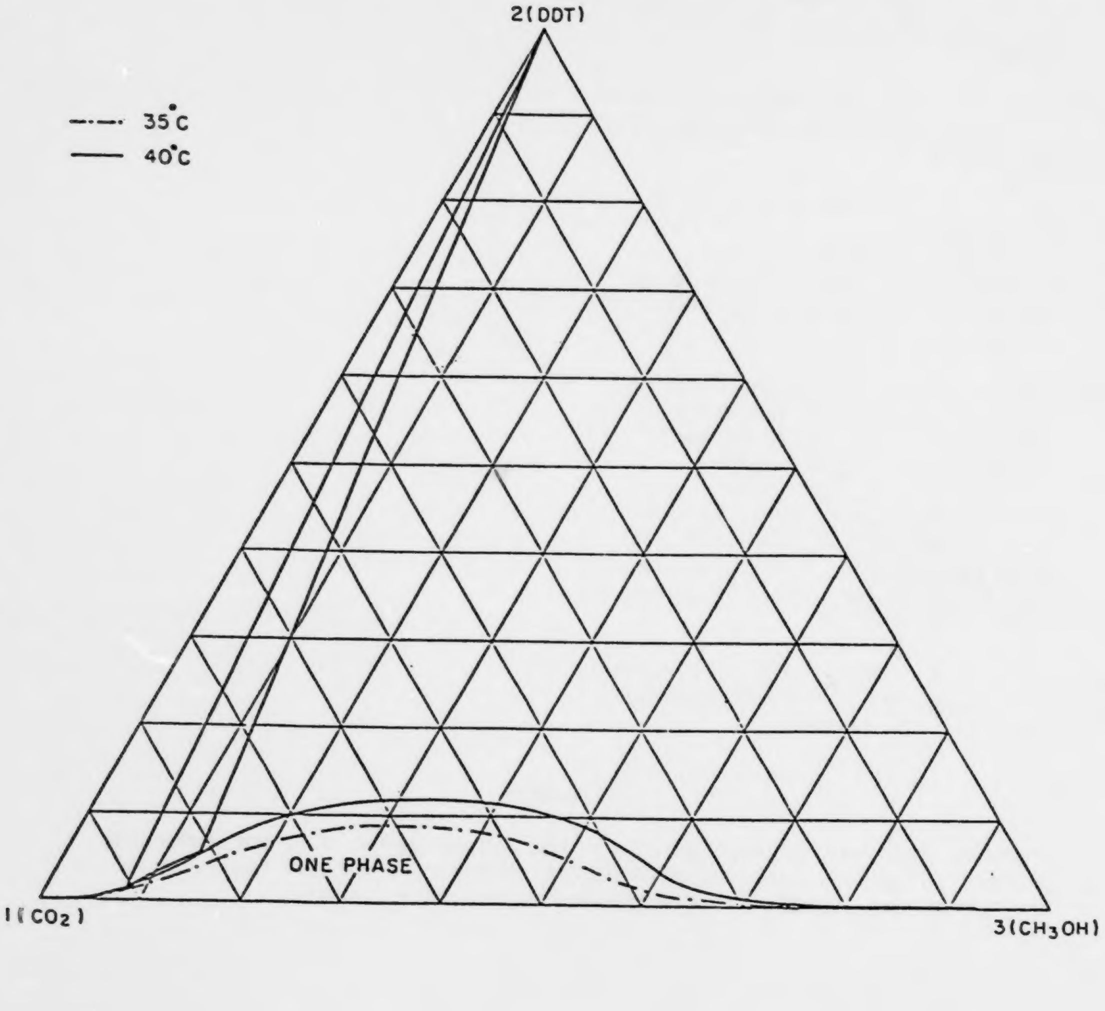


Figure 1. Phase behavior of the ternary system of CO_2-DDT-methanol at 35°C and 40°C, 100 atm.

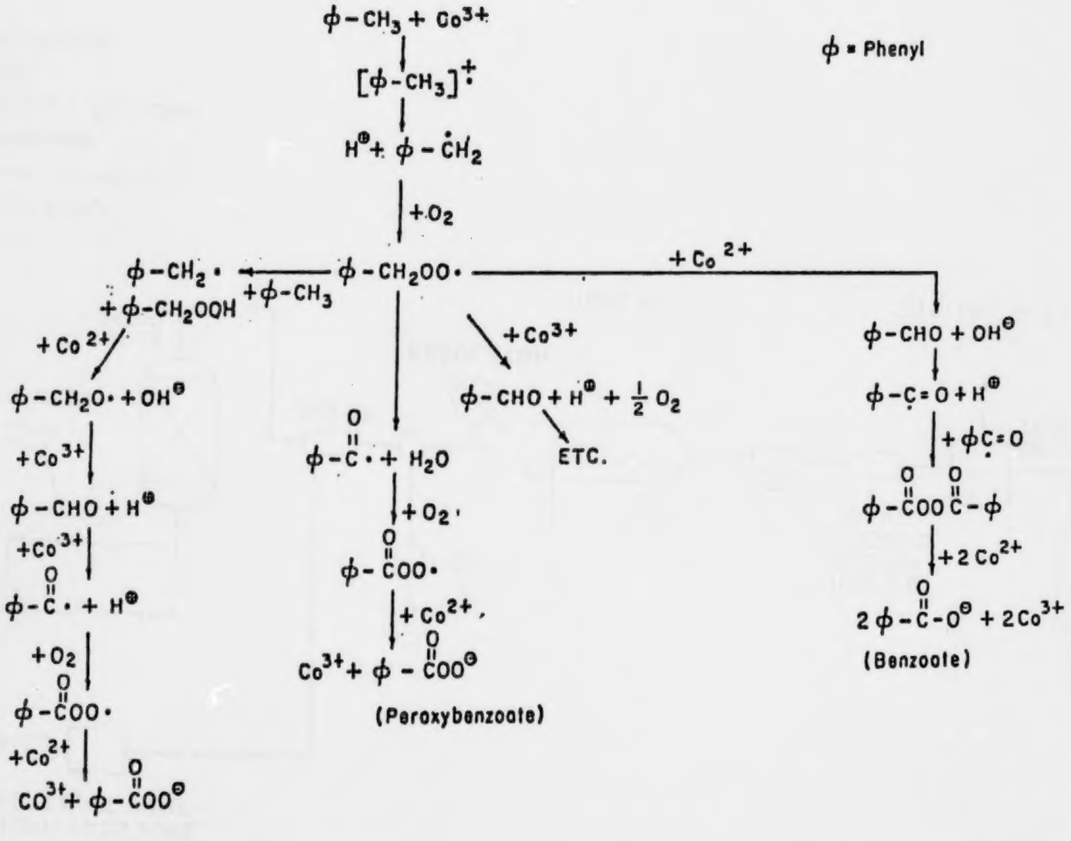

ϕ = Phenyl
ϕ-CH3 + Co3+
[ϕ-CH3]+•
H⊕ + ϕ-ĊH2
+O2
ϕ-CH2OO•
+ϕ-CH3
ϕ-CH2• + ϕ-CH2OOH
+Co 2+
ϕ-CH2O• + OH⊖
+Co3+
ϕ-CHO + H⊕
+Co3+
ϕ-C• + H⊕
+O2
ϕ-COO•
+Co2+
CO3+ + ϕ-COO⊖
ϕ-C• + H2O
+O2
ϕ-COO•
+Co2+
Co3+ + ϕ-COO⊖
(Peroxybenzoate)
+Co3+
ϕ-CHO + H⊕ + 1/2 O2
ETC.
+Co 2+
ϕ-CHO + OH⊖
ϕ-C=O + H⊕
+ϕC=O
ϕ-COOC-ϕ
+2 Co2+
2 ϕ-C-O⊖ + 2Co3+
(Benzoate)

Figure 2. Pathways for toluene oxidation.

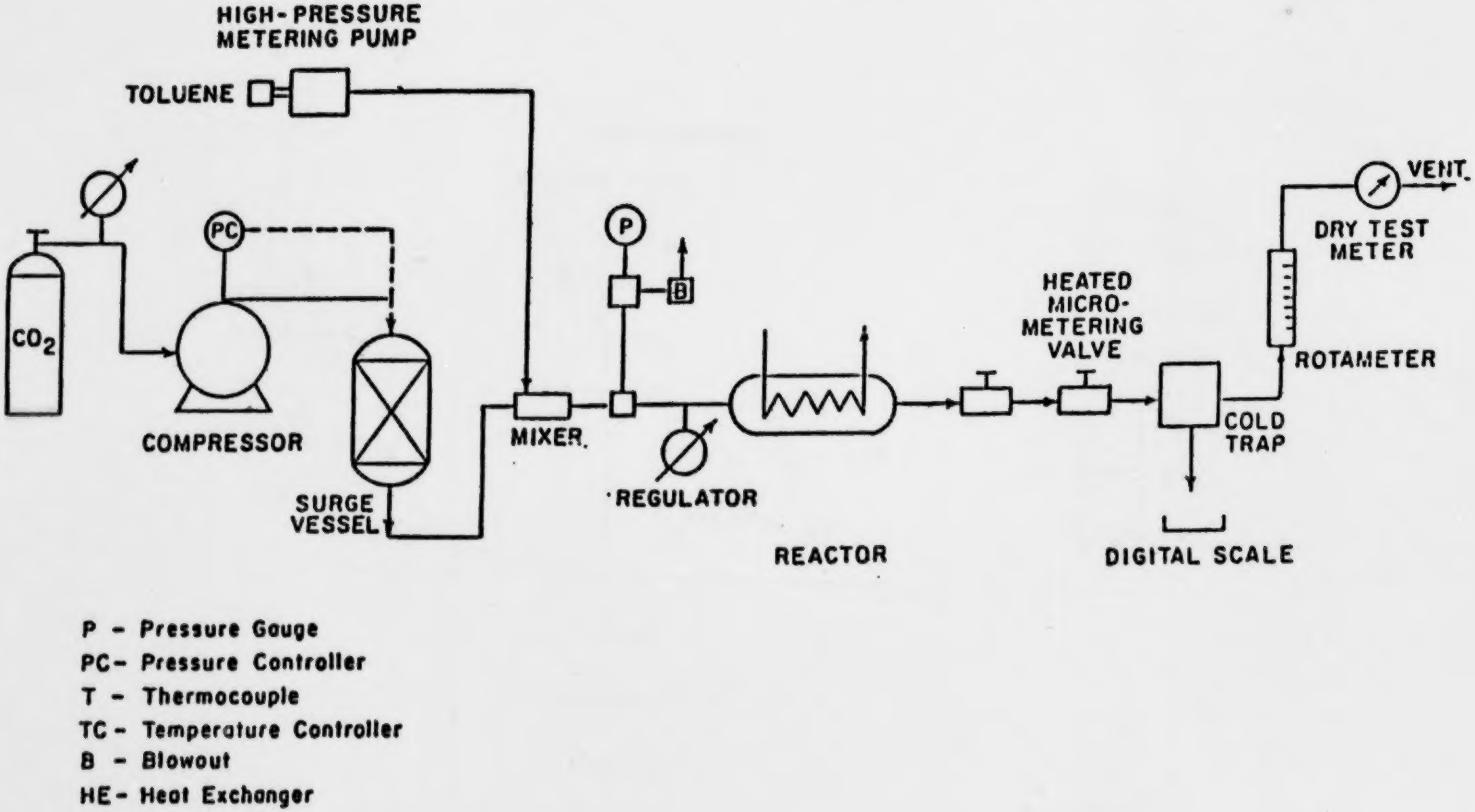

HIGH-PRESSURE METERING PUMP
TOLUENE
CO_2
PC
COMPRESSOR
SURGE VESSEL
MIXER
P
B
REGULATOR
REACTOR
HEATED MICRO-METERING VALVE
COLD TRAP
DIGITAL SCALE
ROTAMETER
DRY TEST METER
VENT
P - Pressure Gauge
PC- Pressure Controller
T - Thermocouple
TC - Temperature Controller
B - Blowout
HE - Heat Exchanger

Figure 3. Schematic of apparatus for supercritical soil extraction

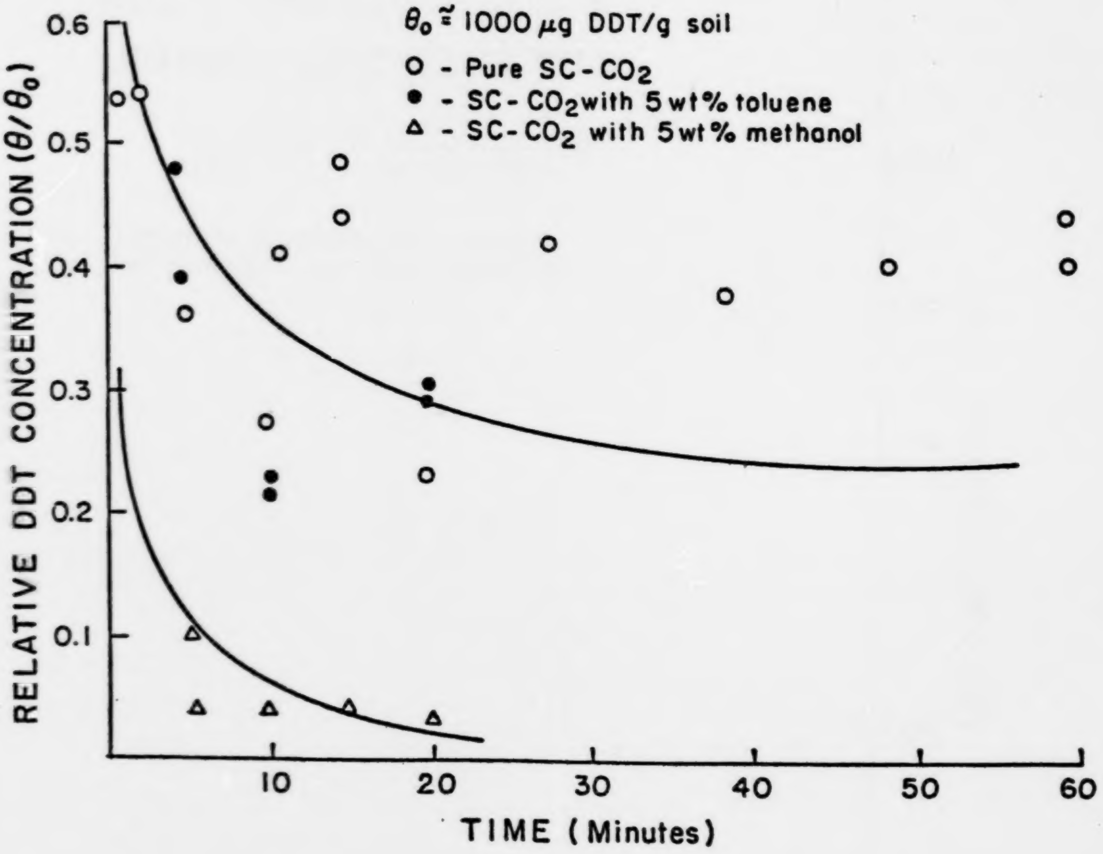


Figure 4. Temporal variation of relative soil concentration in the extraction of a DDT-contaminated, spill-site topsoil, showing the effect of entrainers.

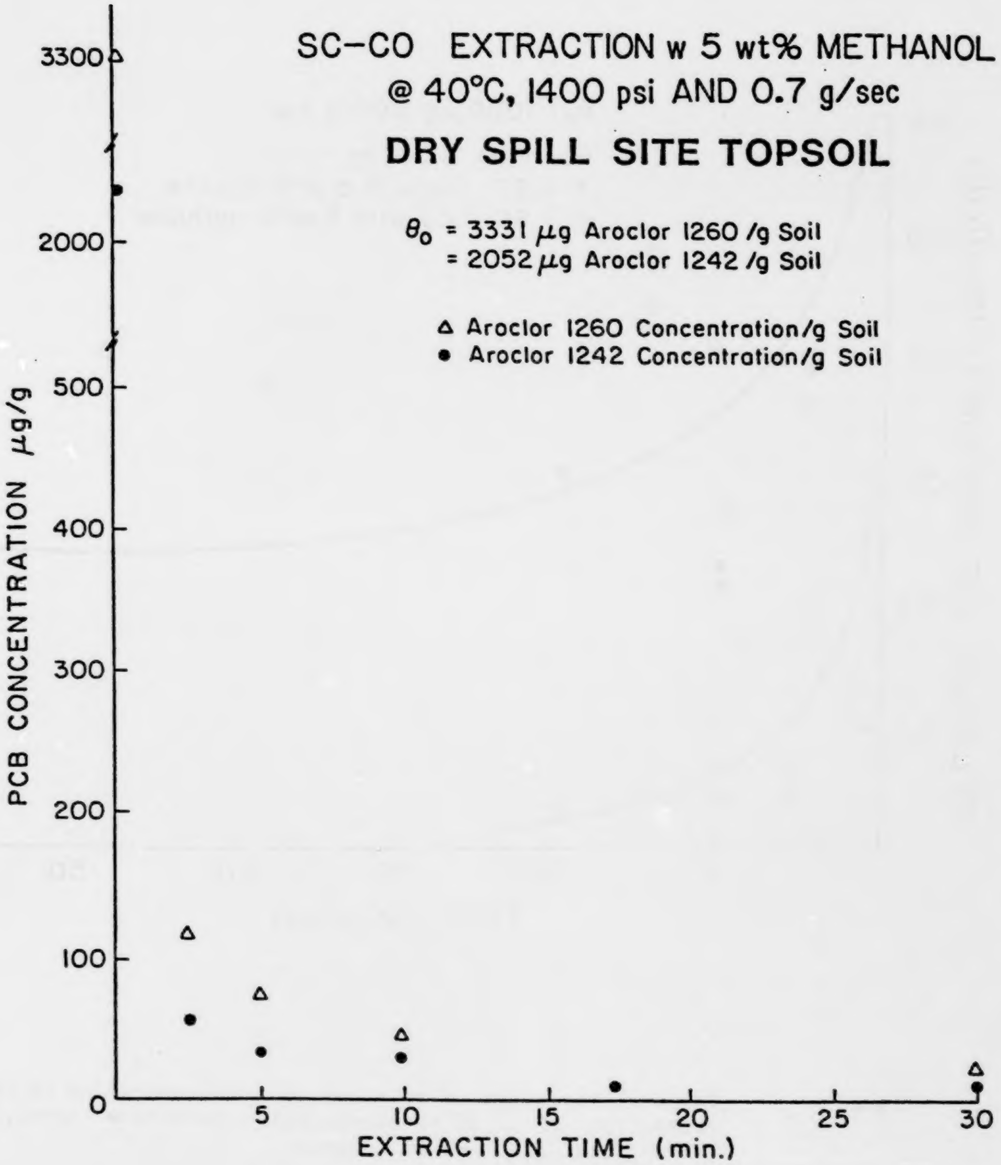


Figure 5. Temporal variation of relative soil concentration in the extraction of a PCB-contaminated, spill site topsoil.

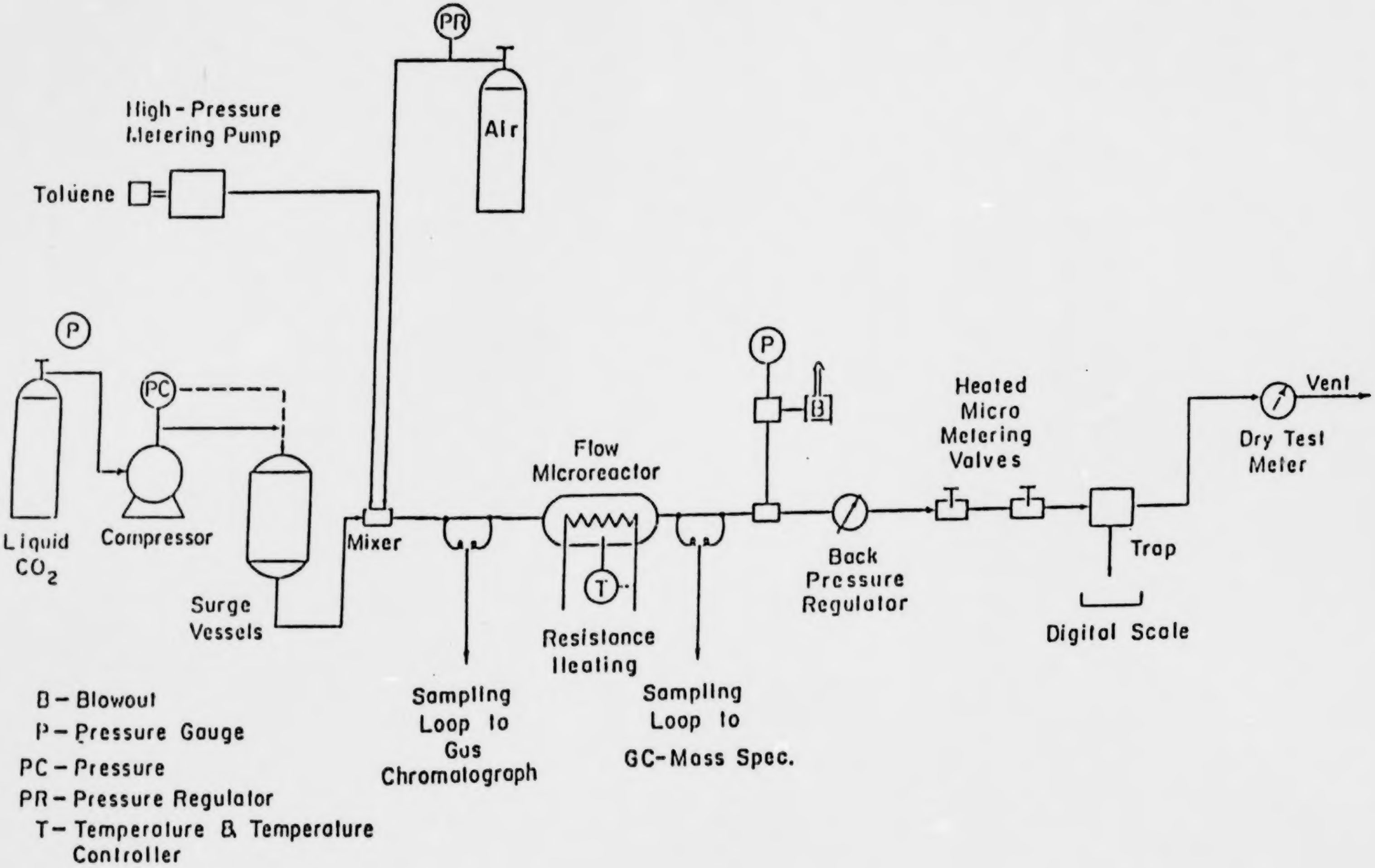

PR
High-Pressure
Metering Pump
Air
Toluene
P
PC
Liquid CO2
Compressor
Surge
Vessels
Mixer
Flow
Microreactor
T
Resistance
Heating
Sampling
Loop to
Gas
Chromatograph
Sampling
Loop to
GC-Mass Spec.
P
B
Back
Pressure
Regulator
Heated
Micro
Metering
Valves
Trap
Digital Scale
Dry Test
Meter
Vent
B – Blowout
P – Pressure Gauge
PC – Pressure
PR – Pressure Regulator
T – Temperature & Temperature
Controller

Figure 6. Schematic of apparatus for SCF reaction studies.

EPA'S PILOT SCALE TREATABILITY STUDIES FOR HAZARDOUS WASTES

Robert A. Olexsey
and
Douglas W. Grosse
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Cincinnati, OH 45268

ABSTRACT

Congress, through the 1984 Hazardous and Solid Waste Amendments, has required EPA to establish treatment standards for wastes that have been traditionally disposed of to the land. Full-scale treatment data from well-designed and well-operated facilities is not available for all wastes. This paper describes the pilot-scale research program at EPA's Hazardous Waste Engineering Research Laboratory in Cincinnati, Ohio. Treatment processes for both organic and inorganic wastes are described. Preliminary test data are presented.

INTRODUCTION

EPA's Hazardous Waste Engineering Research Laboratory (HWERL), located in Cincinnati, has recently launched a substantial intramural research program into the treatability of hazardous wastes by a number of physical/chemical/biological treatment processes. The primary purpose of this pilot plant program is to provide data on the capabilities of treatment alternatives to land disposal. Data from the treatment evaluations will be used by EPA to establish land disposal restriction regulations as required by the Hazardous and Solid Waste Amendments (HSWA) of 1984.

The pilot plant testing described here is being conducted at EPA's Testing and Evaluation (T&E) Facility on the grounds of the Mill Creek Sewage Treatment Plant which is operated by the Cincinnati Metropolitan Sewer District (MSD). The facility is operated under contract by the University of Cincinnati, which provides experimental design and operation, sampling, data evaluation, and reporting. Analytical services are provided by another on-site contractor, EER, and the University of Cincinnati. The T&E Facility accommodates treatment of liquids, sludges, and solids. Pilot-scale combustion research is conducted at EPA's Combustion Research Facility (CRF) in Jefferson, Arkansas, while bench-top combustion research is conducted at the Center Hill Facility in Cincinnati.

Preceding page blank

Treatability studies at the T&E Facility are divided into two areas: organic wastes and inorganic wastes. Wastes of both types can be treated in either the liquid or sludge form.

Plant Layout

Figure 1 describes the layout of the T&E Facility (1). The areas devoted to hazardous waste treatability studies are highlighted. These studies occupy 5 of the 16 high bay areas in the T&E Facility. Remaining bays are utilized for wastewater treatment and land disposal research.

The organic treatment processes include biological treatment (activated sludge), carbon adsorption, steam stripping, steam distillation and thin film evaporation. Inorganic waste treatment processes are neutralization, reduction, precipitation, chemical oxidation, filtration, ion exchange, dewatering, and solidification/stabilization.

Treatability Studies for Organic Wastes

Incineration will be the technology most often applied to concentrated (greater than 10 percent) organic wastes. It has been proven to be an effective technology for a wide variety of wastes. However, incineration is costly and incineration capacity is limited. As a function of waste type and concentration, alternatives to incineration merit attention for organic wastes.

Distillation

Distillation can be applied to concentrated wastes (greater than 10 percent) in circumstances where the intent is recovery of a product or separation of two or more materials for subsequent processing. Steam distillation is the most common form of distillation applied to low boiling point materials, such as waste solvents. Steam distillation can be "direct" in which steam is injected directly into the liquid solution or "indirect" in which steam coils produce the heat to drive the process (2).

The distillation system installed at the T&E Facility, as described in Figure 2, consists of a 125 gallon batch still with a six-inch diameter (I.D.) column that can be raised to 25 feet in height. The still is constructed of stainless steel and is an indirect steam driven unit. The system is equipped with reflux capacity, that is, the ability to recycle product from the condenser into the top of the column to yield higher concentrations of high volatile compounds in the overhead vapor. Distillation will be studied as a technology to treat waste solvents (RCRA waste codes F001-F005). It may also be studied for sludges from wood preserving wastes (K001); chlorinated hydrocarbon wastes (K073); washes and sludges from ink formulations (K086); and others.

Steam Stripping

Steam stripping is a form of simple distillation in which steam is directly injected into a waste in order to separate the more volatile components. Steam stripping is most applicable for treatment of aqueous wastes with an organic concentration below 10 percent. In batch steam stripping, waste is charged into a boiler and steam is injected directly into the waste. The gases which are condensed from a steam stripper contain water

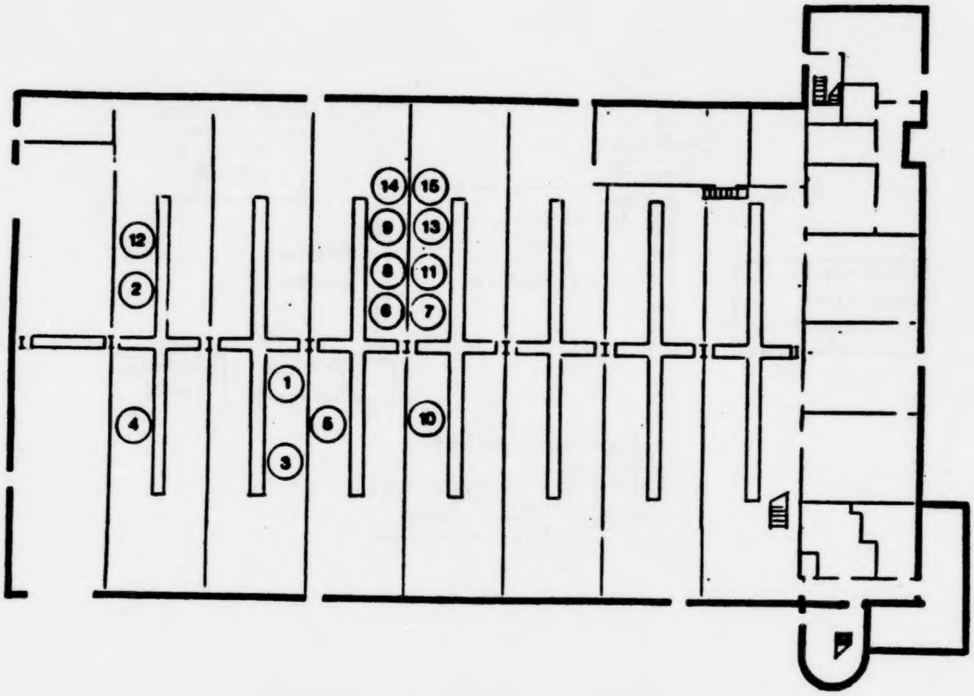


FIGURE 1. HAZARDOUS WASTE TREATMENT PROCESS LOCATION MAP AT EPA'S TEST AND EVALUATION FACILITY

Key to Figure 1

1. Batch Distillation
2. Chemical Oxidation (wet-air oxidation)
3. Steam Stripping
4. Carbon Adsorption
5. Thin-Film Evaporation
6. Precipitation and Neutralization
7. Cyanide Destruction - Alkaline Chlorination
8. Chromium Reduction
9. Sulfide Precipitation
10. Biological Treatment
11. Cyanide Destruction - Ozonation
12. Stabilization and Fixation
13. Inorganics: Ion Exchange
14. Activated Alumina
15. Mixed Media Filtration: Inorganics

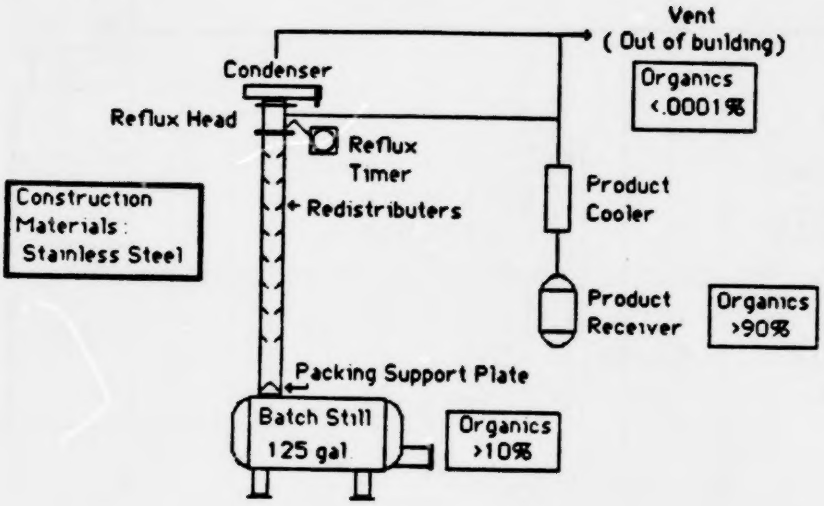

Vent
(Out of building)
Organics
<.0001%
Condenser
Reflux Head
Reflux
Timer
Construction
Materials:
Stainless Steel
Redistributers
Product
Cooler
Product
Receiver
Organics
>90%
Packing Support Plate
Batch Still
125 gal
Organics
>10%

FIGURE 2. BATCH DISTILLATION

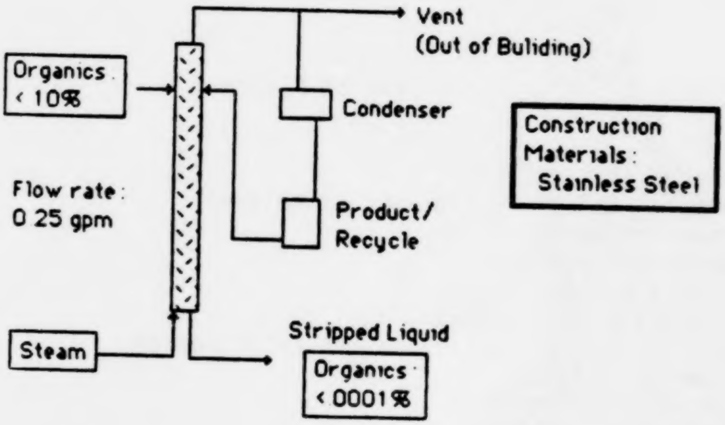

Vent
(Out of Buliding)
Organics
< 10%
Condenser
Construction
Materials:
Stainless Steel
Flow rate:
0.25 gpm
Product/
Recycle
Steam
Stripped Liquid
Organics
<.0001%

FIGURE 3. STEAM STRIPPING

along with the more volatile organic components of the waste in the form of a two-phase mixture. The mixture is decanted and the organic component is drawn off for reuse or disposal. The aqueous layer is fed back to the stripper for further treatment. In continuous steam stripping, waste flows down a column while steam flows up. The column is designed to promote heat transfer from the steam to the waste to cause turbulence in the waste and to create a large surface area. Different liquid-vapor equilibria exist in the column, with the highest relative concentration of the most volatile components found at the top (3).

The EPA pilot facility contains a continuous steam stripper which is described in Figure 3. The column is 2 inches in diameter and contains three sections. The maximum column height is approximately 10 feet. The waste flow rate is up to 0.25 gallons per minute with an initial steam to volatile organics (VO) ratio of 6.5 lb per lb.

Steam stripping is applicable for a wide array of aqueous organic wastes. As part of the EPA treatability studies, steam stripping will be investigated for waste solvents (F001-F005) and for dilute wastes from acrylonitrile production (K011 and K013).

Biological Treatment

A number of biological degradation processes have been used to destroy organic pollutants in industrial and municipal wastewaters. These include activated sludge, aerated lagoons, trickling filters, and stabilization ponds. Activated sludge can be a viable treatment process for aqueous waste containing dilute concentrations (less than 1 percent) of biodegradable organic compounds.

Figure 4 depicts the pilot-scale activated sludge units employed at EPA's T&E Facility. There are currently eight such units installed at the facility. Each unit can accommodate 11 liters per day, with a 10-day sludge retention time (SRT). The reactors and clarifiers are enclosed to facilitate gas sampling. This gas sampling is a critical component of the program since a principal objective of the work is to determine the fate of volatile organic materials in the activated sludge system.

Two of the activated sludge units have been operated on mixtures of pure compounds and water. Table 1 presents performance and fate data for seven runs each for methyl ethyl ketone (MEK) and 1,1,1 trichloroethane (TCA). From Table 1, it is obvious that the MEK was much more biodegradable than was TCA under similar circumstances of the testing. The hydraulic retention time (HRT) for both systems was 24 hours and the sludge wasting rates were set to achieve a target sludge retention time (SRT) of 10 days. The reactors were air mixed using airstone diffusers. Primary, secondary, and reactor off-gases were sampled using borosilicate glass trays packed with Tenax (4).

Future work with activated sludge will be conducted on actual waste solvents and other dilute, biodegradable organic materials.

Other Organics Treatment Processes

In addition to distillation, steam stripping, and biological treatment, other organic waste

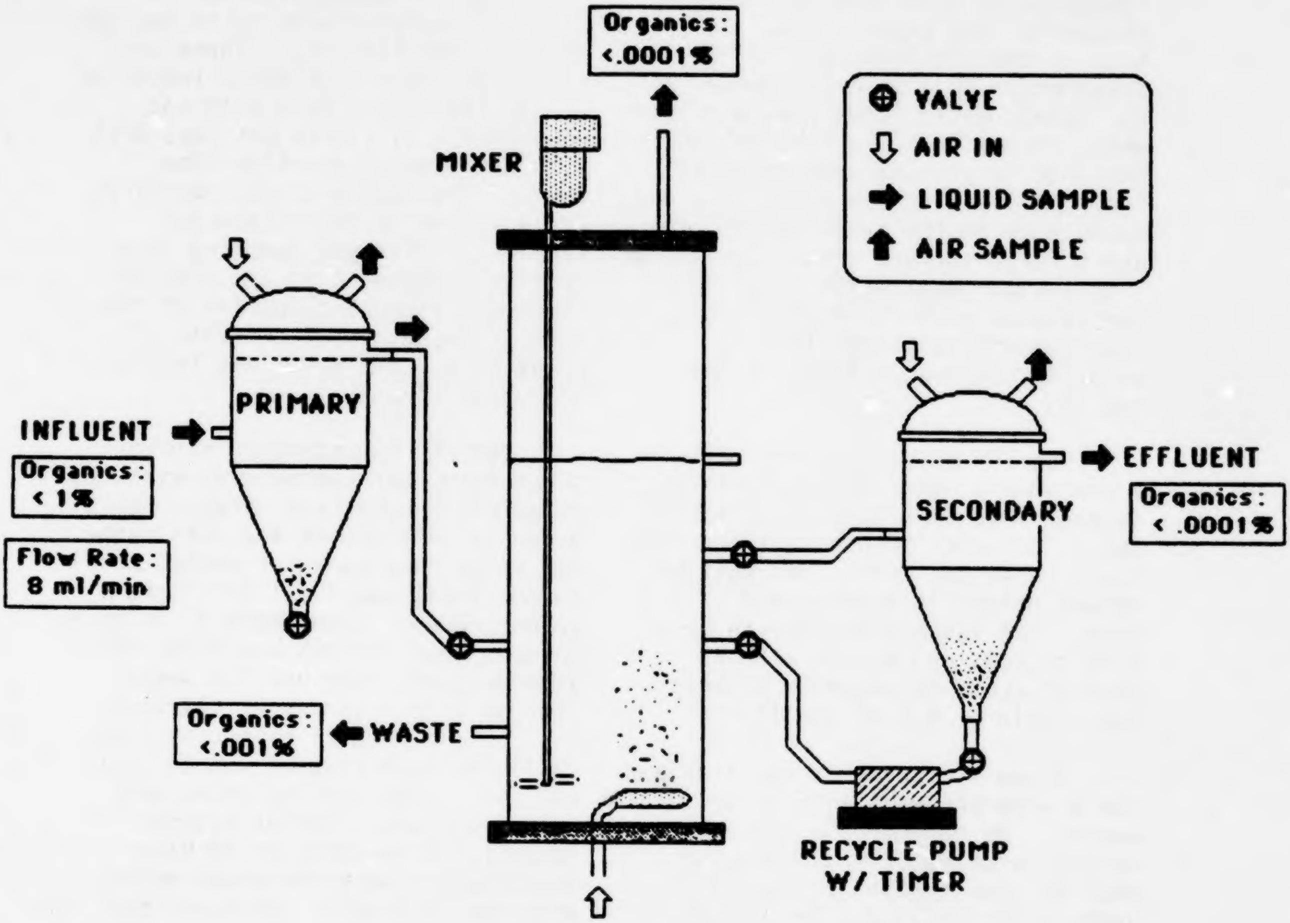

Organics : <.0001%
MIXER
⊕ VALVE
⇩ AIR IN
➡ LIQUID SAMPLE
⬆ AIR SAMPLE
PRIMARY
INFLUENT
Organics : < 1%
Flow Rate : 8 ml/min
EFFLUENT
SECONDARY
Organics : < .0001%
Organics : <.001%
WASTE
RECYCLE PUMP W/ TIMER

FIGURE 4. **Organics: Biological-Activated Sludge**

Table 1. Fates of MEK and TCA in Activated Sludge
(Percent of Influent Mass)

	MEK	TCA
Primary Volatilization	11.0	18.8
Unknown Primary Loss/Gain	-7.5	11.8
Reactor Stripping	5.7	54.0
Secondary Volatilization	0.2	0.5
Waste Sludge	0.1	0.1
Effluent	0.8	2.7
Biodegradation (by difference)	89.7	12.1
Concentrations		
Influent (mg/l)	55	141
Effluent (mg/l)	0.5	3.8

treatment processes at the T&E Facility include evaporation, carbon adsorption, and chemical oxidation. Thin-film evaporation is a technique for concentrating dilute solvent mixtures prior to subsequent treatment (e.g., distillation). Carbon adsorption can be used to treat extremely dilute wastes in aqueous solution or as a polishing step subsequent to biological treatment. Wet air oxidation can be used for aqueous organic wastes that are too dilute for incineration and too toxic for biological treatment.

Treatability Studies for Inorganic Wastes

Many of the large volume RCRA wastes, such as metal finishing wastes, contain corrosives, metals, and cyanides. These wastes, often aqueous, require treatment prior to discharge of the liquids to receiving waterways or sewage treatment facilities. Discharge of these wastes directly to surface impoundments will no longer be an acceptable management technique for these wastes. Treatment residues (sludge) will require dewatering and either fixation/stabilization or removal/recovery of inorganic contaminants prior to land disposal. The technologies that are applicable to treating aqueous inorganic hazardous wastes are very similar to the technologies used to deal with the same contaminants in industrial wastewaters.

Cyanide Destruction

Many metal finishing process streams and wastewaters contain cyanide. The cyanide must be destroyed prior to any additional treatment for removal of metals. The most widely used technology for cyanide destruction is alkaline chlorination. This treatment can be accomplished by direct addition of sodium hypochlorite. In single-stage treatment for cyanide with high concentrations, the cyanide is converted to cyanate. In two-stage oxidation, the resultant products are nitrogen and carbon dioxide (5).

Figure 5 describes the alkaline chlorination process located at EPA's

Cincinnati T&E Facility. The maximum flow rate is 2.5 gallons per minute. The process can be run in one or two stages. Wastes that are suitable for alkaline chlorination are plating solutions and sludges (F006 - F012), lime sludge from coking operations (K060), and miscellaneous cyanide-bearing "P" wastes.

Precipitation

Precipitation, particularly lime precipitation, is the process most employed to remove heavy metals from aqueous wastes. In lime precipitation, lime (in slurry or solutions) or caustic soda is added to the waste as a source of hydroxide ion raising the pH to a suitable level for optimum precipitation of the metal hydroxides. The metal hydroxide forms a floc which is removed by settling or filtration. Effluents and residual wastewaters containing excess hydroxide may require neutralization prior to discharge. Sludges precipitated from treatment may require fixation or encapsulation to mitigate post disposal leachability. The optimum pH for precipitation is different for each metal ion. Typically, hydroxide precipitation is optimum at a pH between 9.5 and 12.

Sulfide precipitation is a process that produces the precipitation of a metal ion as a metal sulfide through contact between a metal ion and a sulfide ion. For specific metals, sulfide precipitation can achieve a higher degree of removal than can lime precipitation. Lime precipitation generally offers the lower cost option of the two.

The T&E Facility has the capability for both lime and sulfide precipitation. Figure 6 depicts the lime precipitation process located at the T&E Facility. Maximum flow rate for the lime precipitation process is 2.5 gallons per minute. Recently, metal plating wastes were treated at the T&E to provide comparisons between lime and sulfide precipitation. Some data from these tests are presented in Table 2 (6). The wastes treated were mixed acid/alkali metal rinse baths devoid of hexavalent chromium and cyanide (D006/D008). The source of the wastes was a local Cincinnati metal finisher. The lime precipitation process consisted of precipitation at pH 9.5, unaided flocculation, and clarification. The sulfide precipitation process consisted of pH adjustment to pH 10.5, sulfide precipitation, polymer aided flocculation, and clarification.

From Table 2, it can be seen that, while the sulfide precipitation process achieved marginally better removal for each metal constituent, neither process was effective for removing the nickel. It is probable that this element was complexed with either ammonia or with some other component of the waste, preventing precipitation. Regardless of whatever treatment process is selected, great care must be taken to avoid chelated metals. Complexed metals should be segregated from other metal-laden wastes and treated separately.

Precipitation is applicable to any aqueous metal-bearing hazardous waste stream that does not contain complexed metals. The selection of lime, sulfide, or any other precipitation process is a function of both the metals present and the removal efficiency required.

Other Inorganic Treatment Processes

In addition to alkaline chlorination and precipitation, a number

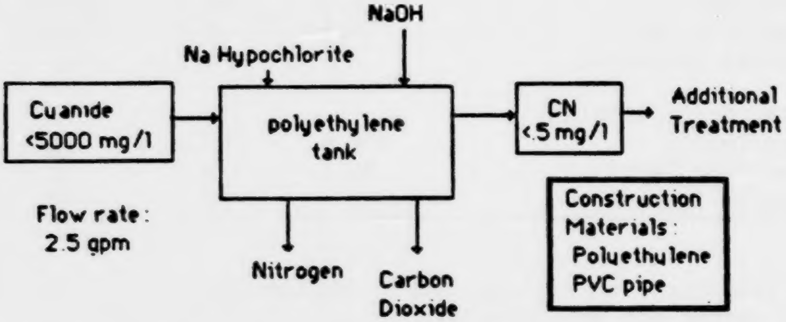

NaOH
Na Hypochlorite
Cyanide <5000 mg/l
polyethylene tank
CN <.5 mg/l
Additional Treatment
Flow rate: 2.5 gpm
Nitrogen
Carbon Dioxide
Construction Materials: Polyethylene PVC pipe

FIGURE 5. CYANIDE DESTRUCTION - ALKALINE CHLORINATION

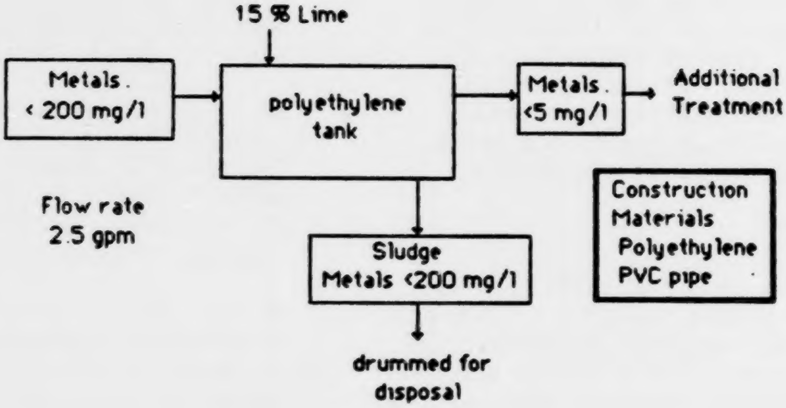

15 % Lime
Metals. < 200 mg/l
polyethylene tank
Metals. <5 mg/l
Additional Treatment
Flow rate 2.5 gpm
Sludge Metals <200 mg/l
drummed for disposal
Construction Materials Polyethylene PVC pipe

FIGURE 6. LIME PRECIPITATION

Table 2. Lime vs. Sulfide Precipitation for D006/D008 Plating Wastes

	Metals			
	Cd	Cr	Ni	Zn
Lime Precipitation:				
Feed (mg/l)	176.5	52.2	128.7	278.8
Clarifier (mg/l)	48.5	6.1	113.7	45.8
Removal (percent)	73	88	12	84
Sulfide Precipitation:				
Feed (mg/l)	194.6	60.1	98.6	415
Clarifier (mg/l)	26.4	3.2	85.3	31.1
Removal (percent)	86	95	14	93

of other processes for dealing with inorganic wastes are available at the T&E Facility. These processes include ozonation, reduction, ion exchange, filtration, and fixation.

Ozonation is a technology that can be used for cyanide destruction either in addition to or in place of alkaline chlorination. Reduction is used to reduce toxic metals (most often chromium) to a less toxic state. Ion exchange, activated alumina, and mixed media filtration can be used to polish liquid effluents after cyanide destruction and precipitation. Fixation, solidification, and stabilization are utilized to treat sludge and solid residues prior to land disposal.

CONCLUSION

At its Cincinnati T&E Facility, EPA has a unique capacity to conduct treatability research on actual hazardous wastes. The facility will be able to conduct research under an EPA Research, Development, and Demonstration (RD&D) permit. Data from this testing will have a significant impact on the land disposal restriction regulations to be promulgated by EPA.

REFERENCES

1. Research, Development, and Demonstration Permit Application, submitted by U.S. EPA, HWERL to U.S. EPA, Region V, November 1986.

2. Turner, Ronald J., "A Review of Treatment Alternatives for Wastes Containing Nonsolvent Halogenated Organics,"Journal of the Air Pollution Control Association (JAPCA), June 1986.

3. Blaney, Benjamin L., "Alternative Techniques for Managing Solvent Wastes," JAPCA, March 1986.

4. Park, J. A., Koczwara, M. K., and Lesiecki, R. J., "Biological Treatment of Aqueous Hazardous Waste," Presented at ASCE National Environmental Engineering Conference, Orlanda, FL, July 1987.

5. Grosse, Douglas W., "A Review of Alternative Treatment Processes for Metal Bearing Hazardous Waste Streams," JAPCA, May 1986.

6. Grosse, D. W., Hassan, S. Q., and Park, J. A., "Treatment of Aqueous Metal Bearing Hazardous Wastes," presented at the AESF/EPA 8th Annual Conference, San Diego, CA, February 1987.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

THE USE OF AIR STRIPPING AND VAPOUR PHASE ADSORPTION PROCESSES FOR THE REMOVAL OF VOLATILE ORGANICS FROM CONTAMINATED GROUNDWATER

by

L. Simovic[1], L.A. Lishman[2] and S.A. Zaidi[1]

[1] Environment Canada, Conservation & Protection, Wastewater
Technology Centre, Burlington, Ontario
[2] McMaster University, Hamilton

ABSTRACT

During the summer of 1986, Environment Canada's Wastewater Technology Centre (WTC) operated a pilot plant at the Gloucester Landfill Site (near Ottawa, Ontario), to treat groundwater contaminated with volatile organic chemicals (VOCs). The plant consisted of a packed air stripping column, with the off-gases being treated by two granular activated carbon (GAC) adsorbers connected in series.

The following VOCs were present: 1,1-dichloroethane, 1,2-dichloroethane, chloroform, 1,1-dichloroethylene, 1,1,1-trichloroethane, benzene, toluene and trichloroethylene.

The study had two objectives: (1) to optimize the operation of the air stripping unit for the removal of VOCs and compare the residuals to the proposed groundwater quality objectives, and (2) to evaluate the effectiveness of GAC adsorbers for the treatment of the off-gas.

Removal efficiencies achieved in the air stripper ranged from 27% - 99.9%, and the optimum conditions identified an air-to-water ratio of 70:1.

Mass transfer coefficients were estimated from the results of the air stripping tests and were compared to the coefficients predicted by the Onda model[1]. They were found to be in good agreement.

For four VOCs, (1,1-dichloroethane, 1,2-dichloroethane, chloroform and benzene) the breakthrough and saturation points were obtained for the first GAC adsorber. At saturation, the GAC loading of the organics was compared to the loading predicted using the Dubinin and Radushkevich equation[2]. These were found to be in good agreement.

In the effluent of the second GAC adsorber, the concentrations of all the compounds were below the lower limit of detection of 2 μg/L.

INTRODUCTION

Leachate from the Gloucester Landfill Site located near Ottawa, Ontario, had contaminated the groundwater in that area with miscellaneous synthetic organics to the extent that wells in the nearby residential area were threatened. The site had been used primarily for disposing of municipal wastes, however, hazardous wastes had been disposed of in an area designated as the "Special Waste Compound". Studies were carried out at this site on the migration of the contaminants[3] and on potential site remedial measures[4,5]. A review of the published information showed that adequate data were not available for the design of an optimum system for the removal of volatile organic chemicals (VOCs) from contaminated groundwater by air stripping (AS). There was also concern about the impact of air stripper off-gases[4]. Consequently, a project plan was developed, a pilot plant was assembled and a seven week field study conducted to collect the missing data.

The concentrations of the VOCs in the effluent from the air stripper were compared to the proposed site groundwater quality objectives[4]. A comparison was made between the calculated AS mass transfer coefficients and those predicted using the Onda model[1] with the intention of using Onda's model predictions to design the full scale treatment plant.

The mass of selected organics adsorbed per unit mass of granular activated carbon (GAC) were determined from the experimental data. These values were then compared with predicted values obtained with the use of a model based on the Dubinin and Radushkevich (D-R) equation[2].

PURPOSE

The objectives of the study were: 1) to determine the conditions under which the maximum removal of selected VOCs could be obtained by AS and compare the residuals to the proposed groundwater quality objectives, and 2) to evaluate the effectiveness of vapour-phase activated carbon adsorption for removing organics from the air stripper off-gases.

APPROACH

Pilot Plant

A schematic of the pilot plant is shown in Figure 1.

The groundwater was pumped, using a 10 cm Reda Submersible pump, into two 1100 L covered tanks. From the tanks, the water was pumped to the top of the air stripper, at a rate of either 8 L/min or 4 L/min, countercurrent to the air flow. The air flow rate and volumetric air-to-water (A:W) ratios were calculated on the basis of maintaining a gas pressure drop of 200-400 N/m^2 per meter of packing. Effluent samples were collected only after the gas and liquid flow rates had stabilized. Based on an initial test, this operating period was determined to be 120 minutes.

Groundwater Used in the Study

Data from several earlier publications[3-6], were reviewed on the concentration of various organics in the samples of groundwater from different wells at the site. The contaminated groundwater for this study was obtained from a new well located about 5 m outside the "Special Waste Compound". Table 1 shows the concentrations of the VOCs, and inorganic parameters in the groundwater used in this study.

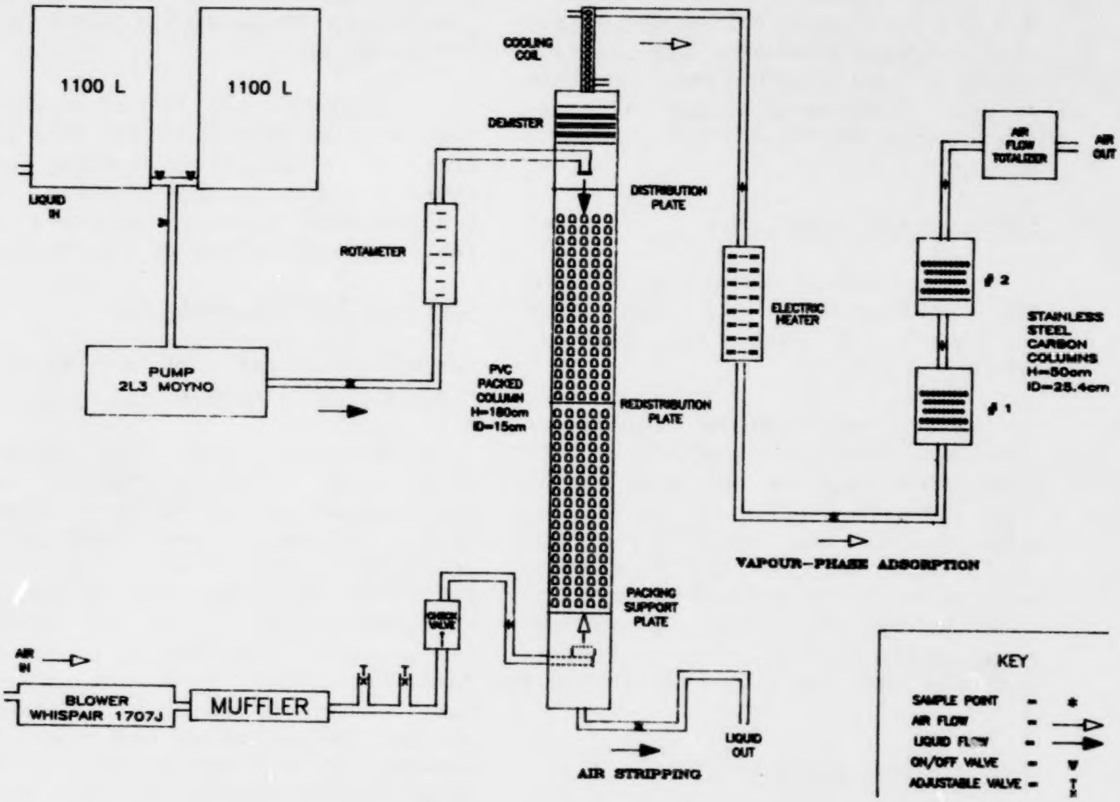

1100 L
1100 L
LIQUID IN
ROTAMETER
PUMP 2L3 MOYNO
COOLING COIL
DEMISTER
DISTRIBUTION PLATE
PVC PACKED COLUMN H=180cm ID=15cm
REDISTRIBUTION PLATE
PACKING SUPPORT PLATE
ELECTRIC HEATER
AIR FLOW TOTALIZER
AIR OUT
# 2
# 1
STAINLESS STEEL CARBON COLUMNS H=50cm ID=25.4cm
VAPOUR-PHASE ADSORPTION
AIR IN
BLOWER WHISPAIR 1707J
MUFFLER
CHECK VALVE
LIQUID OUT
AIR STRIPPING
KEY
SAMPLE POINT - *
AIR FLOW -
LIQUID FLOW -
ON/OFF VALVE -
ADJUSTABLE VALVE -

Figure 1. Pilot Plant at Gloucester Landfill Site.

Table 1. Groundwater Contaminants

Volatile Organics	Conc. Range (μg/L)	Inorganics	Conc. Range (mg/L)
1,1-Dichloroethane	66 - 210	Fe	1.1 - 3.7
1,2-Dichloroethane	370 - 550	Ca	83.1 - 98.9
Chloroform	47 - 203	Mg	26.1 - 28.7
1,1-Dichloroethylene	16 - 180	Al	0.05-0.06
1,1,1-Trichloroethane	9 - 38	Mn	0.04- 0.07
Benzene	69 - 320	Zn	<0.1
Toluene	36 - 133		
Trichloroethylene	26 - 162		

The liquid pH varied between 4.8 and 7.3; total solids concentration averaged 0.33 g/L; air relative humidity (RH) 71.0% (ave.) and the average temperatures for air and liquid were 19.3°C and 17°C, respectively.

Experimental Conditions

The experimental conditions and packing types and sizes used during the AS tests are shown in Table 2.

The vapour-phase adsorption test was carried out after AS process which applied the high liquid flow rate (8 L/min), 1.9 cm Intalox Saddles (IS), and an A:W ratio of 70:1. The GAC used in this study was Calgon's 4x6 mesh BPL, which is used in typical industrial vapour-phase applications. The conditions for this test are presented in Table 3.

Sampling and Analysis

All liquid samples from the AS tests were analyzed for VOCs. Temperature and pH were also measured and recorded. Random samples were analyzed for total solids, calcium, magnesium, iron, zinc, aluminum and manganese.

The influent air and off-gas samples were collected at the start of the air flow and after 120 minutes of operation. At the time of sample collection, temperature, velocity and RH were also measured. The off-gas samples were collected at the inlet to the heater, and at the inlet and outlet of the first and second GAC columns.

Volatile organics in the liquid and gas samples were analyzed by the purge and trap method using a gas chromatograph with a flame ionization detector[7].

Approximately 10% of the samples were submitted to the WTC laboratory in duplicate, along with several standards and blanks. The results were used to estimate the analytical error during the study.

Approach to Data Analysis

Estimation of air stripping mass transfer coefficients

Assuming that no process other than stripping removed compounds from the contaminated groundwater, the overall mass transfer coefficient (K_La) was calculated following Kavanaugh and Trussell's procedure[8]. The values for Henry's Law constant (H), used in these calculations, were from the literature[9]. This constant is considered to be the primary parameter for determining how efficiently a compound can be removed by AS. Since temperature has a strong influence on the value of H, a Van't Hoff-type relation[8] was used to correct H values for the actual temperature used in the tests.

The mass transfer rate coefficient correlation model of Onda[1] that describes counter-current air stripping in a packed tower, was used to predict the values of air stripping mass transfer coefficients for each compound. These predicted values were then compared with the calculated K_La values.

Vapour-Phase Adsorber

The equilibrium loading of individual organics on GAC were estimated using the Polanyi's potential theory[2]. These values were then

Table 2. Experimental Conditions - AS Tests

Packing Type	Packing Size (cm)	Air:Water Ratio	
		Water Flow:8 L/min	Water Flow:4 L/min
Intalox Saddles (IS)	1.3	15	50
		20	70
		30	110
	1.9	20	50
		30	70
		70	110
Raschig Rings (RR)	1.3	15	50
		20	70
		30	110
	1.9	20	50
		30	70
		70	110

Table 3. Adsorption Bed Parameters

Bed Parameters	First Bed	Second Bed
Bed Depth	3.8 cm	3.4 cm
Diameter	25.4 cm	25.4 cm
Density	0.525 g/cm^3	0.526 g/cm^3
Weight of Carbon	989.1 gm	898.7 gm
Void Fraction of Bed	0.382	0.381

applied to a Dubinin-Radushkevich (D-R) equation based model[10] to calculate the amount of a given organic adsorbed per unit weight of GAC in the vapour-phase adsorber used in this study. The calculated amounts were then compared with the values determined from the experimental data.

PROBLEMS ENCOUNTERED

The heater used to increase the temperature and reduce the RH of the air stripper off-gas, did not perform in the field as well as had been expected. The RH, therefore, was reduced only to an average of 62% (21.4°C), instead of the <50% (24°C) as planned.

RESULTS

Air Stripping

The removal efficiencies for all measured VOCs achieved during AS tests ranged from 27%-99.9% depending on the test conditions and the concentrations and characteristics of the compounds. The best removal efficiencies were achieved under the following test conditions: liquid flow rate 4 L/min; packing 1.3 cm IS; A:W = 70:1. These % removals are presented in Table 4 together with the influent and effluent concentrations of the VOCs.

Table 4. Best Removal Efficiencies Observed During AS Tests

	4L/min;1.3cm RR; A:W = 110:1			4L/min;1.3cm IS A:W = 70:1			
Compounds	Concentration (µg/L) Influent	Concentration (µg/L) Effluent	Removal (%)	Concentration (µg/L) Influent	Concentration (µg/L) Effluent	Removal (%)	Proposed* Ground-Water Quality Objectives (µg/L)
1,1-dichloroethane	34	0.3	99.1	99	2.0	98.0	NA
1,2-dichloroethane	76	4.0	94.7	177	10.0	94.3	10
chloroform	30	1.0	96.7	81	3.0	96.3	30
1,1-dichloroethylene	13	0.2	98.5	115	2.0	98.3	0.3
1,1,1-trichloroethane	41	0.1	99.8	24	0.3	98.7	18400
benzene	11	0.1	99.1	107	0.4	99.6	10
toluene	5	0.3	94.0	49	0.3	99.4	14300
trichloroethylene	17	0.2	98.8	81	1.0	98.8	30

* Ref (4)

At higher A:W ratios of 110:1 and by using RR the removal efficiencies were statistically similar.

For economic reasons, the results obtained by using IS (less expensive than RR) and lower A:W ratio (less power required) were considered the optimum. For most VOCs the final effluent concentrations were within the proposed groundwater quality objectives (Table 4). However, these objectives were not met for 1,1-dichloroethylene. In most of the other tests, the concentrations of two compounds, 1,2-dichloroethane and 1,1-dichloroethylene, in the AS effluent exceeded the objectives. With respect to 1,2-dichloroethane, this is understandable since H, for this compound, is quite low $(1.3 \text{ atm m}^3/\text{mol } 10^{-3})$. The objective for 1,1-dichloroethylene was much more stringent than for any other VOC monitored in this study, and often it was difficult to reach. This will have to be taken into account when calculating the depth of the packing for a full-scale system, that may be required to meet the objectives for these two compounds.

An example of the predicted and calculated values for the K_La from the experiment at a flow rate of 4 L/min, 1.3 cm IS and A:W=70:1,is presented in Table 5.

Generally, the predicted and calculated values were in reasonably good agreement. Since the Onda model does not account for end effects in the air stripping column, the differences between predicted and observed values are understandable. In addition, Onda and co-authors did not develop their model for the IS. However, the results obtained during this study and those reported earlier by Lamarche[11] show that the model does in fact predict the K_La values reasonably well for some compounds using IS as the packing. The intention is to use Onda's model predictions in the design of a full-scale treatment plant .

Vapour-Phase GAC Adsorption

In Figures 2a and 2b, the vapour-phase concentrations of the eight observed VOCs in the stripper off-gas (influent to #1 GAC column) are plotted versus the total experimental time of 83 hours. When the detection limit of 2 µg/L was taken into consideration, the influent concentrations of 1,1,1-trichloroethane and toluene (Figure 2a) were at the detection limit and their results with respect to estimating carbon loading were judged to be unreliable.

Removal efficiencies achieved in the #1 GAC column ranged from 88.6% to 99.9%. In the effluent from #1 GAC column, the concentration of trichloroethylene was below the detection limit, and the results of 1,1-dichloroethylene showed too much scatter. Therefore, these data were also not used for estimating carbon loading. Data for the remaining VOCs were used to construct breakthrough profiles for the first carbon adsorber. An example is shown in Figure 3 for 1,2-dichloroethane.

The loadings of the VOCs at the saturation point were determined from the breakthrough profiles and are shown in Table 6. The predicted values for benzene and 1,2-dichloroethane loadings based on the D-R equation are also shown in Table 6.

The observed value for the saturation loading of 1,2-dichloroethane was very close to the predicted value. For benzene, the value is considerably lower, and may be explained by the lower extent of adsorption expected in a multi-component system.

The concentrations of all the VOCs in the effluent of the #2 GAC column were found to be below the lower limit of detection and loadings, therefore, could not be accurately determined.

In summary, the data collected in this study show that AS can effectively remove VOCs from the contaminated groundwater at Gloucester Landfill Site. Optimum design parameters for the AS column were: liquid flow rate 4 L/min; A:W = 70:1 and 1.3 cm Intalox saddles. Under these conditions >94% removal of all VOCs was observed. For a full-scale system, the height of the packing should be chosen to ensure that 1,2-dichloroethane and 1,1-dichloroethylene objectives are met.

Use of vapour-phase GAC adsorber effectively removed all VOCs from the AS off-gas. Data from the study were found to be reasonably consistent with predicted values from the relevant theoretical models.

ACKNOWLEDGEMENTS

The authors would like to thank J.D. Brewer for the assistance provided during the experimental program and preparation of this document, and he and L. Whittle for their assistance in the field. Thanks go to the staff of the WTC Laboratory Services Section for conducting all VOC analyses, and to Transport Canada for their financial support. The cooperation of H. Whittaker and his staff at the Environmental Emergency Technology Division in Ottawa, Ontario was much appreciated.

Table 5. Calculated Mass Transfer Coefficients Compared to Those Predicted by Onda's Model[1]

	$K_La \times 10^{-3}(sec^{-1})$		% Deviation from
Compounds	Calculated	Predicted	Onda's model
1,1-dichloroethane	9.99	8.50	17.6
1,2-dichloroethane	6.98	7.48	6.6
Chloroform	10.11	7.54	34.1
1,1-dichloroethylene	8.94	9.01	0.9
1,1,1-trichloroethane	10.93	7.52	45.3
Benzene	13.41	7.80	71.9
Toluene	13.43	7.80	72.3
Trichloroethylene	11.30	8.15	38.6

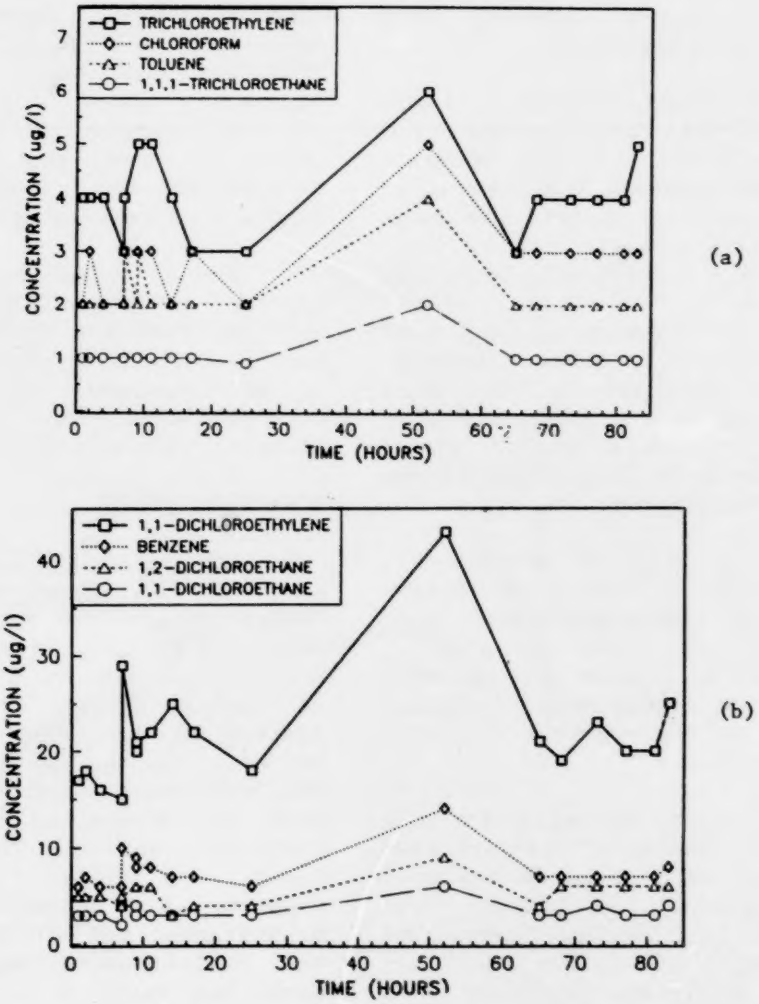


Figure 2a & b. Influent to Carbon Column #1.

Table 6. The GAC Loadings - Actual and Predicted

Compounds	Influent Conc. (µg/L) STP*	Actual (mg/gm C)	Predicted (mg/gm C)
1,1-dichloroethane	3.5	71.50	-
1,2-dichloroethane	6.2	32.86	36.69
Chloroform	3.5	30.15	-
Benzene	9.3	51.62	78.68

* Standard temperature (0°C) and pressure (1 atm)

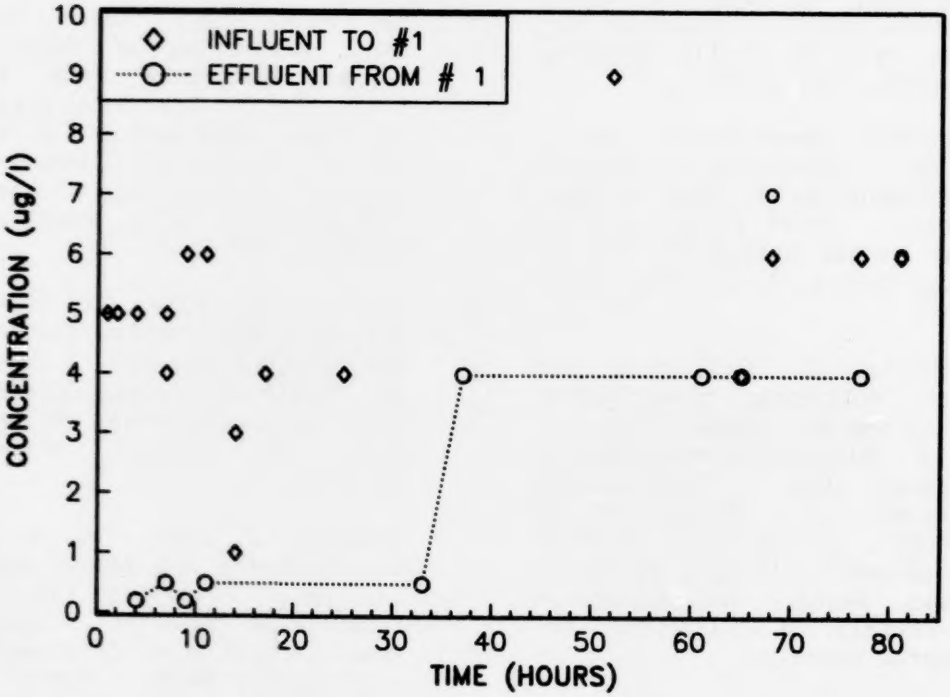


Figure 3. Breakthrough Profile for 1,2-dichloroethane
= #1 Carbon Column

REFERENCES

1. Onda, K., H. Takeuchi and Y. Okumoto, 1968. Mass Transfer Coefficients Between Gas and Liquid Phases in Packed Columns, Journal of Chemical Engineering of Japan, 1:1, pp.56-62.

2. Reucroft, P.J., W.H.Simpson, and L.A.Jonas, 1971. Sorption Properties of Activated Carbon, The Journal of Physical Chemistry, 75, No.23.

3. Jackson, R.E., J.M. Bahr, D.W. Belanger, and S. Walbridge, 1985. The Gloucester Project: A Study in Organic Contaminants Hydrology, presented at the Second Canadian/American Conference on Hydrogeology, Hazardous Wastes in Ground Water: A Soluble Dilemma, held in Banff, Alberta, Canada, June 25-29.

4. Canviro Consultants Ltd., 1984. Treatment of Organic Contaminants in Landfill Leachate. Final report submitted to the Wastewater Technology Centre, Burlington, Ontario.

5. Simovic, L., J.P.Jones and I.C. McClymont, 1986. Physical/Chemical Removal of Organic Micropollutants from RO Concentrated Contaminated Groundwater. Proceedings of HMCRI's 3rd National Conference and Exhibition on Hazardous Wastes and Hazardous Materials, p.120, March, Atlanta, Georgia.

6. Simovic, L., J.P.Jones, 1987. Removal of Organic Micropollutants from Contaminated Groundwater by Oxidation and Stripping. Accepted for publication in the Water Pollution Research Journal of Canada, Vol. 22, No.1.

7. U.S.EPA, 1984, Federal Register, 40 CFR Part 136, Oct.26.

8. Kavanaugh, M.C. and R.R. Trussell, 1980. Design of Aeration Towers to Strip Volatile Contaminants from Drinking Water. Research and Technology Journal AWWA, 0003-150X/80/120684, Dec.

9. Warner, H.P., J.M.Cohen, and J.C.Ireland, 1980. Determination of Henry's Law Constants of Selected Priority Pollutants. Municipal Environmental Research Laboratory, Office of R&D, U.S. EPA, Cincinnati, Ohio. 45268.

10. Cortright, R.D., 1986. Gas-Phase Adsorption of Volatile Organic Compounds From Air Stripping Off-Gas Onto Granulated Activated Carbon - A Thesis for Master of Science in Chemical Engineering, Michigan Technological Univ. Houghton, Michigan, USA.

11. Lamarche, P., 1986. Air Stripping Mass Transfer Correlations for Volatile Organics, A Thesis for Master of Applied Science, Chemical Engineering, University of Ottawa, Ottawa, Ontario.

12. Simovic, L., 1987. The Use of Air Stripping and Vapour Phase Adsorption Processes for the Removal of Volatile Organics from Contaminated Groundwater - Gloucester Study - report in preparation, the Wastewater Technology Centre, Burlington, Ontario.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency.

CHEMICAL DESTRUCTION OF CHLORINATED DIOXINS AND FURANS*

Charles J. Rogers & Alfred Kornel
Hazardous Waste Engineering Research Laboratory
26 W. St. Clair Street
Cincinnati, OH 45268

ABSTRACT

There existed in 1982 an estimated 415 commercial wood preserving plants in the U.S. generating daily a total of nearly 5.5 million gallons of process waste. The process waste contains both toxic organics such as chlorinated phenols, dioxins, furans and the metals, copper, chromium, arsenic and zinc, rendering it difficult to treat conventionally. The pentachlorophenol purchased by industry to treat wood normally contains 100-200 ppm heptachlorodibenzo-p-dioxins (HCDD) and 1000-25000 ppm octachlorodibenzo-p-dioxins. Recent analyses have revealed that the highly toxic tetra-chlorinated dioxins and furans were present in 9000 gallons of collected waste on a wood preserving site in Butte, Montana. In January 1986 laboratory studies were conducted to determine if potassium polyethylene glycol reagents (KPEGs) could be used to destroy, by dehalogenation, all chlorinated dioxin (PCDD) and furan (PCDF) homologs in 9000 gallons of light petroleum oil collected previously from groundwater. Results from the laboratory studies revealed that PCDDs and PCDFs could be destroyed to non-detectable levels under conditions of 100°C for 30 minutes. Arrangements were made to implement the chemical treatment of oil in a 2700 gallon mobile reactor system. The chemical treatment was successfully completed in July 1986.

INTRODUCTION

The enormous variety and amount of toxic halogenated organic materials which have pervaded our environment during the past fifty years have left us with major, crucial problems of disposal. These problems were clearly delineated in a recent U.S. EPA publication (1). The accumulation of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs, "dioxins") in soil, sediment, and living tissue is a serious problem that has received considerable public OCDD, and with the high temperatures and pressures involved, there exists the possibility that the more toxic tetra-chlorinated dioxins and furans may be formed. Of the disposal options available, the majority of the wood preserving plants practiced storing the waste water on site and relying on evaporation to reduce waste to sludge.

Conventionally, the "clean up" of such contaminated sites usually involves landfilling and is not really a permanent solution but rather a transfer of a toxic waste from one region to another. Landfilling is now curtailed under the 1984 RCRA amendments.

---

*Cofunded by the USAF Engineering and Services Center, Tyndall Air Force Base, Florida.

The chemical stability of PCDD, PCBs and other haloorganics precludes their destruction by conventional refuse incineration methods. Most municipal incinerators cannot achieve the high temperatures necessary to destroy these chemicals in waste. Mobile incinerator technology has been developed for on-site treatment of waste. However, early estimates are that on-site incineration of toxic waste at a wood preserving site will be costly.

Currently, some commercial chemical methods are used to chemically alter or destroy PCBs and other haloorganics in contaminated oils and attention in recent years. As an example, there exist an estimated 415 commercial wood-preserving plants in the U.S. generating daily a total of nearly 5.5 million gallons of process waste which contains toxic materials (2). The pentachlorophenol (PCP) products purchased by industry to treat wood normally contain 100-200 ppm heptachlorodibenzop-dioxin (HCDD) and 1000 to 25000 ppm octachlorodibenzo-p-dioxins (OCDD). Also, preliminary investigations of dioxins showed that in the use of PCP with these high concentrations of HCDD and soils. The chemical methods developed by Acurex, Goodyear, and Sun Ohio involved dispersion of metallic sodium in oil or the use of sodium-biphenyl or naphthalene mixtures. Because of the reactivity of sodium with water, these reagents cannot be used efficiently to directly decompose PCDDs or PCBs in soils, sludges, sediments and dredgings. Other chemical reactions have been evaluated for dehalogenation of environmental pollutants but have not been found to be adaptable to field conditions (3,4,5).

Biological treatment of PCDDs, PCBs and other hazardous pollutants is also receiving attention. The efficacy of microbes to destroy toxic halogenated compounds has not been fully evaluated by U.S. EPA or independent laboratories.

During the summer of 1978 a new chemical reagent was synthesized and used to effectively dechlorinate PCB-contaminated oils (6). Since that time a series of reagents have been prepared from potassium hydroxide and polyethylene glycol (KPEGs) which, with heating, produce rapid dehalogenation of haloorganic compounds (7,8,9,10).

In 1982 detailed investigations were initiated to determine the effects of variable reaction parameters on the rate and extent of chemical decontamination of soils (11). This research focused almost exclusively on the direct chemical treatment of PCDD-contaminated soil. The most recent investigation, initiated in January 1986, was aimed at identifying treatment conditions for chemical destruction of PCDDs and PCDFs in oil stored on a wood preserving site in Butte, Montana (12).

PURPOSE

Research and field investigation studies were initiated in January 1986 to determine if a chemical reagent prepared from potassium hydroxide and polyethylene glycol could be used to treat PCDD and PCDF contaminated oil at a wood preserving industrial site near Butte, Montana. The wood preserving site contained approximately 9000 gallons of light petroleum oil collected previously from groundwater over a period of two years. The oil contained 3.5% pentachlorophenol, PCDD and PCDF homologs ranging from 422 ppb of tetra-isomers to 83,923 ppb of octa-isomers. Because of the presence of these highly toxic chlorinated dioxins and furans, the oil could not be transported off-site for incineration. Bringing in and operating a mobile incinerator for on-site destruction of contaminated oil was rejected because of high costs.

In April 1986, U.S. EPA Region VIII agreed, after review of laboratory data, that the chemical process, based upon a potassium polyethylene glycol (KPEG) reagent, could be used to decontaminate on-site the PCDD/PCDF contaminated oil.

The basic mechanisms of KPEG reagents used in these processes have been already determined for both halogenated aliphatic and aromatic compounds (6,14).

APPROACH

Procedure

Initial treatment experiments with some of the PCP waste-contaminated samples obtained from Butte, Montana were accomplished on January 9, 1986. For these tests, two 500-ml samples were obtained, one an oil waste (the EPA designation was "Cut, 41266-4-10") and the other a contaminated soil (the EPA designation was "Yard, 41266-1-8"). The procedures utilized for the treatment of the oil samples with the KPEG reagents are described in the following:

- Aliquots of oil samples (24.94 grams) were removed from the container and accurately weighed into new, pre-cleaned 125-ml sample bottles fitted with Teflon-lined caps. A reagent blank bottle was simultaneously prepared.
- Twenty-five (25) grams of the KPEG reagent were added, at ambient temperature, to each of the three sample bottles mentioned above.
- The bottles were placed in sand baths maintained at temperatures of 70°C and 100°C for a period of 8 hours and the contents of each bottle were stirred with a motor-driven stirring rod during this entire period.
- Accurately weighed aliquots (typically 1-5 grams) of the sample were removed from the reactor at intervals of 15 minutes and placed in 125-ml flint glass bottles. The destruction reaction which had been occurring was quenched by adding a sufficient quantity of 50% H_2SO_4 to each bottle to adjust the pH to about pH 7, as determined by indicator paper.

Following quenching of the treated samples, the bottles were set aside until test portions could be successfully extracted and analyzed (12).

Extraction and Analysis of PCDD and PCDF from the Sample Matrix

The procedures for extraction and analysis of PCDD and PCDF were based on adding appropriate internal standards to each aliquot taken from the reaction. At a minimum, 1-2 ng each of 2,3,7,8-[$^{13}C_8$]-TCDD, 2,3,7,8-[$^{37}Cl_4$]-TCDD and 2,3,7,8TCDF were added to each 125-ml flint glass bottle containing 1-5 grams of the treated oil sample. Sample extracts were prepared and were analyzed using DB-5 capillary GC columns to obtain data on the concentrations of PCDDs and PCDFs. Perkin-Elmer Sigma II or Varian 3740 GCs were used for the analysis. The Kratos MS-30 Mass

Spectrometer was used in the low resolution mode to detect PCDDs and PCDFs. If PCDDs and PCDFs were detected, a second portion of the sample extract was analyzed using high resolution MS (12).

RESULTS

The oil samples obtained from the Butte, Montana site were treated as described with KPEG and were analyzed by GC MS to determine if PCDDs and PCDFs had been destroyed as required by the regulation to less than 1 ppb. Table 1 shows that many of the congeners of PCDD and PCDF were destroyed effectively by the KPEG with a temperature as low as 70°C for 15 minutes. All PCDD and PCDF congeners were completely destroyed by KPEG when the sample was heated to 100°C for 30 minutes. As a result of the successful laboratory tests, arrangements were made to lease equipment to treat the remaining oil stored on the site (13).

The field equipment used to process the oil consisted of a 2700-gallon reactor mounted on a 45-foot trailer equipped with a boiler, cooling system, a laboratory and a control room. Heating of the oil and reagent is achieved by recirculating the oil and KPEG via a pump, a high shear mixer, through a shell and tube heat exchanger. The heat transfer fluid on the shell side of the heat exchanger is heated using a boiler or cooled through a series of radiator type air coolers. The PCDD- and PCDF-contaminated oil was treated in five batches, each consisting of 1400 to 2000 gallons, and required 600 gallons of KPEG reagent per batch. The mixture was heated to 150°C and allowed to react for one and one half hours before cooling. The treated oil was pumped out of the reactor and into a holding tank to confirm by subsequent analysis that PCDDs and PCDFs in the oil had been destroyed below detection limits.

The data from the sampling and analysis of each tank revealed that all PCDDs and PCDFs were destroyed to below the 1 ppb detection limit. The treatment cost was only 10% of the projected incineration cost.

Table 1. LABORATORY-SCALE TREATMENT OF OIL

Contaminants CDD/CDF	Concentration in Untreated Oil (ppb)	Concentration in Treated Residue (ppb) 70°C, 15 min.	100°C, 30 min.	*MDC
TCDD (2,3,7,8-)	28.2	-	-	0.65
TCDD (total)	422	-	-	0.37
PeCDD	822	-	-	0.71
HxCDD	2982	-	-	2.13
TCDF (2,3,7,8-)	23.1	12.1	-	0.28
TCDF (total)	147	33.3	-	0.35
PeCDF	504	-	-	0.36
HxCDF	3918	4.91	-	0.76
HpCDF	5404	5.84	-	1.06
OCDF	6230	-	-	2.62

---

*Minimum detectable concentration in parts per billion.

In August 1986 the equipment was transported to Kent, Washington at the request of U.S. EPA Region 10 and was used successfully to treat approximately 8000 gallons of 2,3,7,8,-TCDD-contaminated liquid waste discovered on an industrial hazardous waste disposal site.

Currently, a new, improved 1 to 2-cubic yard reactor, designed to treat both liquids and solids, is being constructed. In early 1987, field verification studies will be conducted with this new KPEG reactor on four selected PCDD/PCDF- and PCB-contaminated sites. In 1987, it is expected that the KPEG process can be demonstrated to be cost-effective when used at wood preserving and Superfund sites to destroy toxic halogenated pollutants in liquids, sediments, sludges and soils.

ACKNOWLEDGEMENTS

Dr. Thomas O. Tiernan and Staff, Brehm Laboratory, Wright State University, in cooperation with EPA HWERL, treated the oil samples and provided the analytical services under a U.S. EPA contract (Viar Co. SAS NO 1724-X).

The testing of KPEG to destroy PCDDs and PCDFs was co-funded by the Department of the U.S. Air Force, Headquarters Air Force Engineering and Services Center, Tyndall Air Force Base, FL. Captain Edward Heyse was the U.S.A.F. Project Officer.

REFERENCES

1. Edward G. and W. Eisenberg, IIT Research Institute, Treatability of Carcinogenic and Other Hazardous Compounds, EPA-600/2-79-097.

2. Wilson, D., Summary Status of The Wood Preserving Industry, EPA Food and Wood Products Branch Internal Report, 1982.

3. Miller, J., Nucleophilic Aromatic Substitution, Elsevier Press, Amsterdam, 1968.

4. Yoshikozu, K. and S. L. Regen., J. Org. Chem. 1982, Vol. 47, No. 12, 2493-2494.

5. Andrews, A., P. Cremonesi, P. Del Buttero, E. Licondra, and S. Malorano, Nucleophilic Aromatic Substitution of $Cr(Co)_3$-Complex Dihaloarenes with Thiolates, J. Org. Chem. 1983, 48, 3114-3116.

6. Pytlewski, L. L., A Study of The Novel Reaction of Molten Sodium and Solvent with PCB's - U.S. EPA Grant. #R806659010, 1979.

7. Kornel, A., C. J. Rogers, PCB Destruction: A Novel Dehalogenation Reagent, J. Hazardous Materials, 12 (1985) 161-176.

8. Peterson, R. L., Method For Decontaminating Soil, Patent Number 4,574,013, March 4, 1986.

9. Brunelle, D. J. and D. A. Singleton, Chemosphere, 12, (2), 1983, 183-196.

10. Li, and H. Alper, Poly (ethylene glycol) Promote Reactions of Vinylic Dibromides. Dehydrohalogenation and Palladium - Catalyzed Formal Oxidative Homologation. J. Org. Chem. 1986, 51, 4354-4356.

11. Rogers, C. J., Chemical Treatment Of PCBs In the Environment, EPA-600/9-83003, 197-201.

12. Tiernan, T., et al., Wright State University, Dayton, Ohio, Interim Report on the Assessment of Chemical Reagents for Destruction of

Higher PCDD/PCDFs. Internal Report prepared for U.S. EPA, April 15, 1986.

13. Peterson, R., Potassium Polyethylene Gycol Treatment of PCDD/PCDF - Contaminated Oil In Butte, Montana. IT Corp./Galson Research Corp., Project #86-706, July 1986.

14. Rogers, C. J., A. Kornel, Chemical Destruction of Halogenated Aliphatic Hydrocarbons, U.S. Patent Application Serial No. 883,785, Sept. 1984.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

SUPERCRITICAL EXTRACTION OF CONTAMINANTS FROM WATER AND SOIL WITH TOXICOLOGICAL VALIDATION

T.R. Irvin[3], E.K. Stevens[2], R.K. Roop[1], A. Akgerman[1,*]
[1]Department of Chemical Engineering
[2]Department of Veterinary Anatomy
Texas A&M University
College Station, TX 77843

ABSTRACT

Recent attention has been directed to supercritical fluid extraction as a viable method for the economic removal of toxic organic contaminants from hazardous waste streams as well as surface and groundwater resources. In the case of contaminated water resources containing a single toxic agent, the thermodynamics of extraction as well as the distribution coefficient can easily be determined by direct concentration measurements. This method, however, proves unusable in waste sites containing hundreds of toxics of unknown identity; complex mixtures of waste contaminants also prove difficult to separate and characterize by classical chemical methods. Classical mixture thermodynamics cannot thus be used in determining and predicting the distribution coefficient for specific compounds contained in toxic environmental mixtures.

We have used various toxicity indices to determine these two parameters for extraction of complex contaminant mixtures from water and soil. Our approach is to monitor and measure (before and after extraction) water borne toxic activity via application of short term bioassays for three toxic endpoints: carcinogenicity, neurotoxicity, and prenatal/birth defects. The extraction process is carried out in a single equilibrium stage extractor and continued until equilibrium is reached. This approach permits simultaneous determination of a lumped overall distribution coefficient (K value) for the toxic mixture and the extent of extraction necessary for the clean-up of contaminated water or soil. In addition, this novel approach, for the first time, relates the engineering parameters (such as pressure, temperature, superficial velocity, etc.) of the extraction process to toxicity indices.

INTRODUCTION

Recent national attention has focussed on future health and environmental hazards derived from the large quantities of toxic waste chemicals (halogenated aromatics hydrocarbon solvents, oils, petrochemicals, and process chemicals) produced by current and past manufacturing industries. National surveys of hazardous waste generation sites have reported over 14,000 installations generating RCRA-regulated wastes and over 5,000 facilities treating, storing, or disposing of hazardous waste under RCRA-regulating controls. These surveys found over 80 billion gallons (297 million metric tons) of hazardous wastes are produced in the US per year - more than 10 times the quantity of waste for which waste treatment facilities exist. Evidence of the growing quantity of hazardous industrial waste - and growing shortage of industrial capacity for hazardous waste reclamation - is the exponential growth in federal expenditures for toxic waste site cleanups; current estimates target federal expenditures at over 300 million dollars to clean up just 80 major US waste sites, leaving over 10,000 remaining US hazardous waste sites for future attention.

Sharpening public debate on waste issues is the emerging realization that serious toxic waste problems will accompany the development of many new technologies heralded as new sources of industrial growth toward the year 2000. These include:

1. toxic solvents employed for semiconductor chip manufacturing (trichloroethylene, trichloroethane),

2. toxic, specialty chemicals produced in support of electronics and fiber optics manufacture (glycol ethers, hydrazines),

3. toxic solvents for recovery of recombinant DNA-derived pharmaceuticals (hexanes, chloroform), and

4. toxic waste salts derived from industrial gases (arsenes, phosgenes, diboranes).

Public attention on these toxic waste issues has in turn engendered renewed federal and industrial interests in accelerating the development of new, environmentally safe technologies for toxic chemical disposal and elimination. Current methods of waste chemical disposal, such as incineration or landfill storage, have proven unreliable or politically not feasible for routine toxic chemical elimination.

Current methods for toxic chemical elimination also do not address a principal, emerging issue regarding human health hazards from leaking hazardous storage facilities - contamination of surface and groundwater supplies. Recent revelations regarding groundwater quality near semiconductor manufacturing facilities in Silicon Valley, California illustrate the coordinate water quality problems potentially caused by continued misstorage of waste chemical products. Repeated incidences of water source contamination in the Silicon Valley area by industrial solvents engendered an Underground Chemical Waste Tank Analysis by the State of California in which 80 hazardous waste test sites were routinely monitored for waste chemical leakage. Of these sites, 64 (80 percent) indicated subsurface contamination of soil or groundwater, and 57 (70 percent) indicated immediate hazard of drinking water contamination; toxic contaminants identified in these monitoring studies included solvents, acids, toxic metals, resins, and fuels that had leaked from product and raw material storage tanks, waste chemical tanks, fuel tanks, and piping systems. Rapid spot checks of storage tanks at other semiconductor manufacturing plants throughout the country confirmed similar water contamination problems elsewhere. Future public health problems will not only stem from leaking wastes at pasts sites, but also from poorly regulated hazardous waste holding sites from emerging industries.

One promising new technology permitting volume reduction and subsequent disposal of toxic chemicals in water supplies as well as solid waste facilities is the application of supercritical fluids as processing media. Supercritical fluids, fluids that are heated to temperatures above their critical temperature and compressed beyond their critical pressure, offer excellent potential in environmental engineering applications. To date, three approaches have been proposed to employ supercritical fluids to extract toxic substances from water and solid waste (1):

(i) a two step process in which organics are adsorbed onto an adsorbent such as activated carbon with adsorbent regenerated by subsequent extraction with supercritical fluids (2,8).

Two step processes typically utilize activated carbon filters to adsorb water-borne organic contaminants. Nonpolar organic contaminants physically adsorb to carbon surfaces whereas polar compounds chemically adsorb to the polar sites. Since activated carbon or other adsorbent media are expensive, they must be regenerated after saturation with organics; steam stripping, thermal regeneration, and extraction by supercritical fluids are the regeneration techniques most often used. Since no single technique can remove all the chemisorbed toxic substances, eventually adsorbed filters must be replaced and disposed; thus problems associated with filtered toxic chemicals, now adsorbed to an inert matrix, are simply transformed into a solid waste problem (3).

(ii) reactive separation whereby supercritical fluids simultaneously dissolve toxic materials and serve as reaction media (6,7).

During reactive separation, toxic chemicals are dissolved and oxidized in supercritical water at conditions where most inorganics are insoluble in water (6,7). Organics are reformed at severe supercritical conditions and oxidized by added air or pure oxygen; the heat or reaction during oxidation of reformed organics is partly used to heat water as well as to raise solution temperature causing deposition of inorganics. In addition to the difficulties associated with this process in terms of inorganics deposition (3), supercritical water is extremely corrosive requiring special materials for construction. Supercritical conditions necessary to generate supercritical water are also rather severe ($T_c = 374.2°C$ and $P_c = 218.3$ atm) necessitating high capital expenditures.

(iii) a single step process in which the toxic organic contaminants are extracted from water by supercritical fluids.

The broad range of organic solutes which can be extracted from aqueous systems by supercritical fluid extraction (SCFE), as well as the availability of nontoxic extractants such as CO_2 and freons, directed our attention to this process as a viable, economic method for removing toxic organic waste present in industrial waste steams, surface water reservoirs, and ground water reserves. We have applied SCFE to remove toxic organics from water demonstrating that single components as well as toxic organic mixtures can rapidly and effectively be removed from water by SCFE with CO_2.

PURPOSE

Two factors underly current problems in the design, equipment scale-up, and online usage of SCFE systems to eliminate waste toxic compounds in industrial process, waste streams, groundwater supplies, and hazardous waste sites:

1. determination of single overall lumped design parameters for extraction processes, e.g. measuring an overall distribution coefficient (K value) for contaminants distributed between aqueous and supercritical fluid phases, and

2. determination of the extent of extraction required to ensure waste detoxification for a particular toxicant or toxicant mixture, e.g. how much toxin must be removed from contaminated water supplies to ensure safety for human usage.

Supercritical carbon dioxide, with or without entrainers such as methanol, has been employed in these studies principally because of it's favorable chemical properties: non-toxicity, non-flammability, low cost, and low critical point. The fundamental thermodynamic property needed for design and scale up of CO_2-mediated SCFE is the distribution coefficient, defined as the ratio of the mole fraction of the solute in the extract to the mole fraction of the solute in the raffinate. Distribution coefficients for a system containing a single solute can be determined relatively easily by measuring solute concentration in each phase via radioactive tracers or gas chromatographs. In a system which contains more than one solute, however, distribution coefficients for each solute (which are interdependent) must be determined; this task increases in complexity for complex mixtures such as contaminated waste water that could contain many dissolved organic species. Chemical engineers have, traditionally, approached the determination of mixture properties by the lengthly and costly method of determining pure component properties and applying mixing rules. An alternative approach considers the mixture as a single "lumped" or psuedo component and directly applies simple three component extraction principles. One critical parameter for this alternative analysis method is the reliable determination of the mixture concentration in the solvent. We have employed a short term toxicity bioassay to obtain acute toxicity indices directly proportional to mixture concentration. Application of this approach not only provides a "lumped" distribution coefficient for the mixture, but also defines the exact extent of extraction necessary leaving nontoxic levels of mixture components.

The major inhibiting factor in the use of toxicity parameters inconjunction with engineering parameters for design purposes is the lack of quick, accurate toxicity tests. Traditionally the toxicity of a hazardous waste sample has been determined by chemical analyses of the mixture for its components (i.e. GC-MS), doing whole animal studies on the single components, and investigating the synergistic effects of binaries, ternaries, etc.. This is, however, very expensive and time consuming. What is needed, ideally, is a test which can determine the toxicity of a waste stream (before and after a specific cleaning method has been applied) quickly, accurately, and inexpensively.

We have developed such an assay for on-line monitoring of toxic effects of waste chemical produced as byproducts of manufacturing and engineering activities. Specifically, prenatal toxicity and birth defects have been targeted. The large number of incidences of birth defects as well as infant deaths, spontaneous abortions, stillbirths, and miscarriages caused by defective fetal development has directed our attention to this area. We have reported the successful culture of postimplantation rodent embryos for the identification of prenatal toxic and dysmorphogenic components of complex toxic mixtures. Incubation of mixture samples with embryos in culture has proven competent to assess the overall prenatal effects of these mixtures as well as to identify specific mixture components responsible for overall mixture toxicity (4). Applications reported to date include the identification of prenatal toxic components of heterocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, and phenolic petroleum wastes (5). Of the characteristics measured in the postimplantation rodent embryo culture, mortality and crown to rump length (physical length of embryo) were chosen as model indices for lethal dose and toxic dose, respectively. Characteristics such as somite number and yolk sac circulation are toxic indicators also measured in the embryo culture that could be used as well. Other toxic properties besides birth defects, such as carcinogenicity and neurotoxicity, will be addressed in the future. Indices provided by these tests will be used inconjunction with those from the embryo culture to provide a wide range of parameters to validate the use of supercritical extraction.

Creosote, a complex mixture of phenols and polycyclic aromatics isolated from coal tars or beechwood trees, was chosen as a model complex mixture. The outstanding insecticide and fungicide properties of these phenol mixtures previously resulted in extensive creosote use as a wood preservative. A large number of former wood preserving establishments, however, now list among the superfund sites because of creosote contamination. We have chosen creosote as a model environmental toxicant for our studies for this reason.

A toxic aqueous solution was prepared by vigorously mixing water and pure beechwood creosote (Matheson, Coleman, & Bell, lot # 330, 344113), letting the two phases separate, and extracting the saturated aqueous phase. The single stage high pressure equilibrium extractor employed in this study, shown in Figure 1, was charged with 150 cc of the creosote contaminated water and supercritical carbon dioxide to the desired pressure and temperature (system temperature was controlled to within 0.5 K). Vessel contents were vigorously mixed during extraction for 30-45 minutes followed by a one hour period for phase separation. Our previous studies had shown this sufficient to reach equilibrium. During mixing as well as at equilibrium, 0.3 ml samples of the water phase were taken for analysis. The enclosure was subsequently charged with additional supercritical carbon dioxide to a higher pressure, and the entire procedure was repeated. Analysis of water before and after each stage of extraction permits determination of the distribution coefficient as a function of pressure.

Specific details of the postimplantation rodent embryo culture are given elsewhere (4). Nulliparious, female Sprague Dawley rats (225 - 250 grams) were obtained from Harlan-Sprague Dawley Labs (Houston, TX) and breeding was performed. Eleven days after conception, each rat was etherized and embryos removed with yolk sacs intact. Groups of 10 embryos were placed in 15 ml of media mixture which contains 7.5 ml Waymouths 752/1 media, 7.5 ml of frozen rat serum, 1500 units of penicillin, 1500 micrograms of streptomycin, and 2 μl of toxin. They were incubated for 24 hours in a roller culture apparatus set on 40 revolutions per minute. The embryos were then examined for mortality and crown to rump length as well as other embryotoxic indices.

Application of the postimplantation rodent embryo culture provides indices for mortality as well as for various levels of toxicity. A sample of the original toxic solution was tested by the assay to determine the mortality rate and toxicity of the pure sample. Subsequent tests were done on dilutions of the original toxic sample ranging from pure sample to pure water, and the responses were plotted against the dilution. The characteristics of such a plot are shown in Figure 2. Index #1 (the mortality index) exhibits a strong positive response at higher concentrations of solution, decreases, and reaches control levels at some lower concentration "A". Index #2, which is a more sensitive toxicity index, gives a positive response at concentrations of about "A" (some overlap may occur), decreases, and reaches control levels at some lower concentration "B". This trend will be repeated at lower concentrations for other indices of greater sensitivity.

RESULTS

A sample of the original creosote saturated water was tested using the postimplantation rodent embryo culture and exhibited a strong positive mortality response (all embryos died as monitored by lack of heart beat or yolk sac circulation). Dilutions of the original toxic mixture were made with water, ranging from pure toxic solution to one part in one-hundred parts water, and were tested using the embryo culture. A calibration curve was obtained by plotting the normalized mortality and crown to rump length responses for these dilutions, as shown in Figure 3. At about a 6:4 dilution of the aqueous solution, the mortality reached control levels (no embryos died). At about this same dilution, crown to rump length deviated considerably from control levels. Control levels were reached when the dilution was decreased to about 1:9.

The single stage SCFE unit was then used to extract 150 ml of the nondiluted toxic aqueous solution using CO_2. Initially, the extractor was pressured to 500 psi, well mixed, left to separate, and the aqueous phase sampled. This was repeated at several pressures up to 1600 psi at room temperature. The samples were then tested using the postimplantation rodent embryo culture bioassay. The mortality rate is shown in Figure 4 as a function of pressure (at constant temperature). CO_2 saturated with water reaches supercritical conditions at about 1100 psi, and therefore a nondetectable amount of extraction of organic contaminant was accomplished below this pressure. A preliminary gas chromatogram of creosote has shown it to contain over 200 components. At pressures lower than 1100 psi, some of the more volatile compounds may be extracted, however, removal of these compounds does not reduce the toxicity of the aqueous solution. Appreciable removal of the toxic components began at a threshold pressure of about 1300 psi, where the mortality rate deviated from 100 %. A sharp decrease in mortality occurred as the CO_2 underwent large density changes and at 1600 psi, control levels were being approached.

Comparison of the pressure response (figure 4) and the calibration curve (figure 3) reveals that using a single stage equilibrium extractor at 1600 psi will reduce the mortality to 20%, which corresponds to a dilution ratio of 7:3 (30% reduction). It is possible to determine the extent of extraction necessary to adequately clean the water and a "lumped" distribution coefficient from this information. If the solution was sent to a second extractor, another 30% reduction in concentration would occur and similarly for additional extractors added in series. Since control levels are reached at a dilution ratio of 1:9, we conclude that approximately six theoretical stages are required to adequately remove the toxic components. We have assumed that equal amounts of extraction will occur in each stage. Since creosote is a complex mixture with many components of differing volatility, this will not be exactly true and therefore is only an approximation.

The "lumped" distribution coefficient is defined as the ratio of the moles of creosote in the CO_2 per total moles of CO_2 to the moles of creosote in the aqueous phase per total moles of water. This can be rearranged to the form:

$$K = \left(\frac{1-x}{x}\right)\left(\frac{\text{total moles water}}{\text{total moles carbon dioxide}}\right)$$

where x is the ratio of the moles of creosote in the water phase to the total moles of creosote. This ratio is needed since the total moles of creosote is unknown. The original aqueous solution and the aqueous sample at 1600 psi exhibit a toxic response that correspond to 10:0 and 7:3 dilution, respectively, on the calibration curve. This difference represents a 30% reduction in creosote saturated water and hence a 30% reduction in pure creosote concentration. Therefore, 70% of the creosote remains in the aqueous phase so that $x=0.7$. The total moles of water is known from the amount of solution added (assuming the toxin is dilute). The total moles of CO_2 is determined by accurate volume measurement of the extraction vessel. Therefore, all of the parameters required to calculate a K value at 1600 psi are known. The resulting value for the "lumped" distribution coefficient is 1.1.

We have presented a novel approach to determining engineering design parameters from toxicity indices obtained from a short-term bioassay. Through this approach we are able to determine the distribution coefficient for a complex mixture without undertaking lengthly traditional methods for determining mixture properties, as well as the extent of extraction necessary for successful removal of detectable levels of toxin from a solvent. The use of SCFE as a viable means of toxic contaminant removal from a solvent has been substantiated.

REFERENCES

1. Eckert, C. A., J. G. Van Alsten, T. Stoicos, Environ. Sci. Technol., 20(4), 319(1986).
2. DeFilippi,R. P., R. J. Robey, "Supercritical Fluid Regeneration of Adsorbents", Project Summary, EPA-600/52-83-038, EPA, Washington, D.C., 1983.
3. Groves, F. R., Jr., B. Brady, F. C. Knopf, CRC Crit. Rev. Environ. Control, 15(3), 237(1985).
4. Irvin, T. R., A. Akgerman, "Development of Postimplantation Rodent Embryo Culture Systems for Identification of Developmental Toxins and Toxin Fractions in Complex Chemical Mixtures", Chapter in Short-Term Bioassays in the Analysis of Complex Environmental Mixtures - IV, M. D. Waters, Editor, Plenum Press, in press 1986.
5. Irvin, T. R., Mertes, P. C.,Hess, R. K., and Akgerman, A., Proc. Tissue Culture Assn, (1986), 142.
6. Modell, M., R. C. Reid, S. Amin, U.S. Patent No. 4,113,446, 1978.
7. Modell, M., U.S. Patent No. 4,338,199, 1982.
8. Pricht, R. D. et al., AIChE Symp. Ser., 78, 136(1982).

Disclaimer

The work desribed in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

FIGURE 1. Experimental Assembly for Supercritical Extraction.

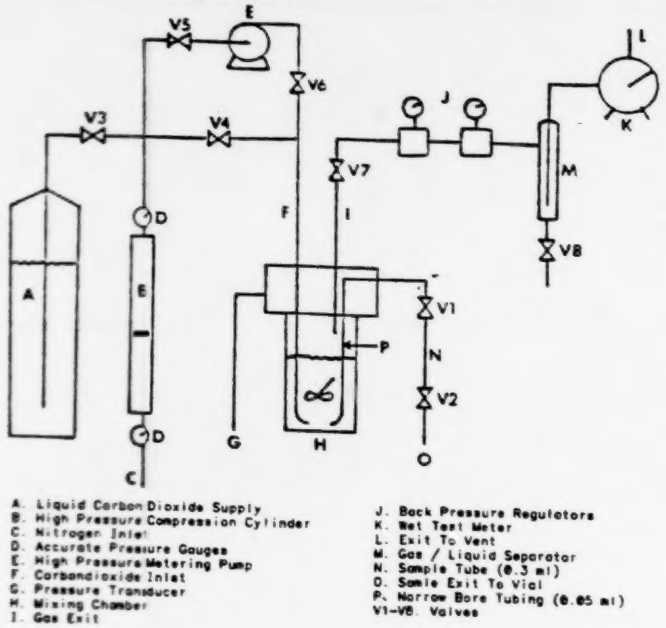

E
V5
V6
V3
V4
J
L
K
M
V7
F
I
D
A
B
V8
V1
P
N
V2
D
G
H
O
C
A. Liquid Carbon Dioxide Supply
B. High Pressure Compression Cylinder
C. Nitrogen Inlet
D. Accurate Pressure Gauges
E. High Pressure Metering Pump
F. Carbondioxide Inlet
G. Pressure Transducer
H. Mixing Chamber
I. Gas Exit
J. Back Pressure Regulators
K. Wet Test Meter
L. Exit To Vent
M. Gas / Liquid Separator
N. Sample Tube (0.3 ml)
O. Samle Exit To Vial
P. Narrow Bore Tubing (0.05 ml)
V1-V8. Valves

FIGURE 2. CALIBRATION CURVE FOR AQUEOUS TOXIC SOLUTION

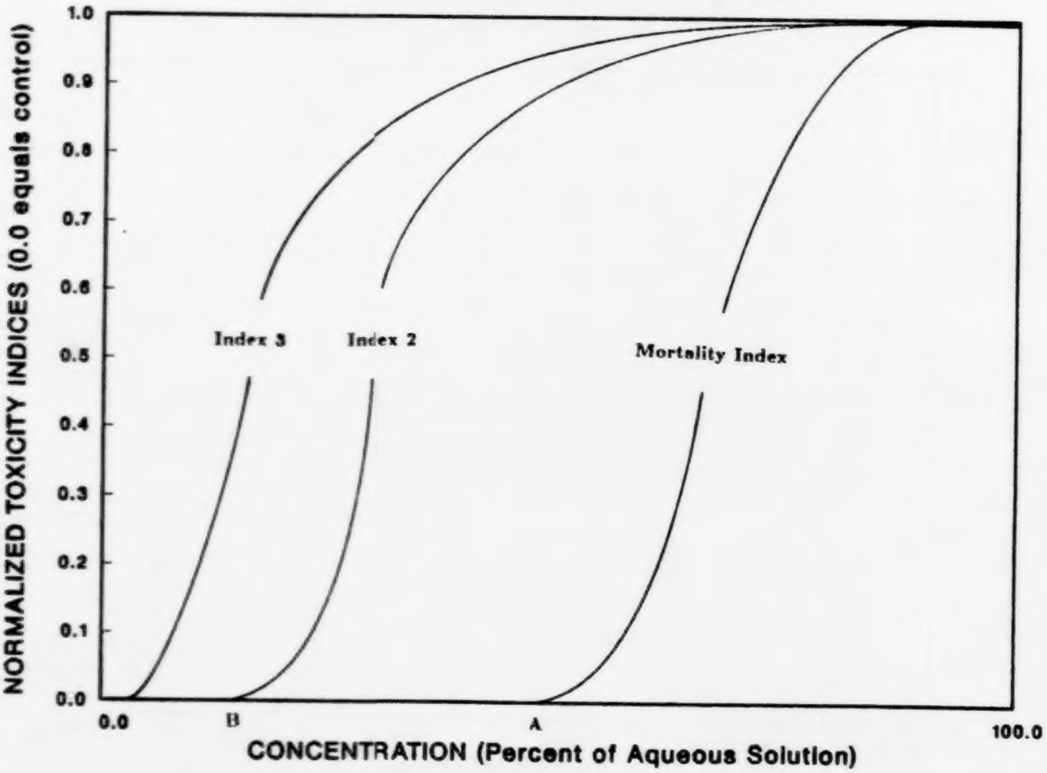


FIGURE 3. CALIBRATION CURVE FOR CREOSOTE SATURATED WATER

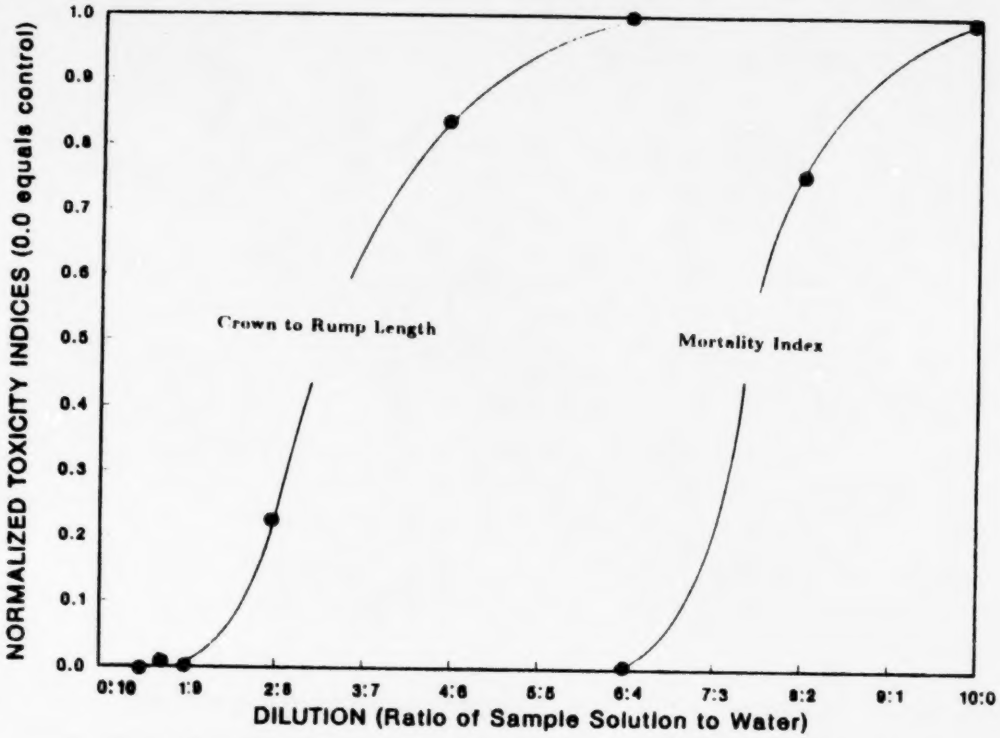
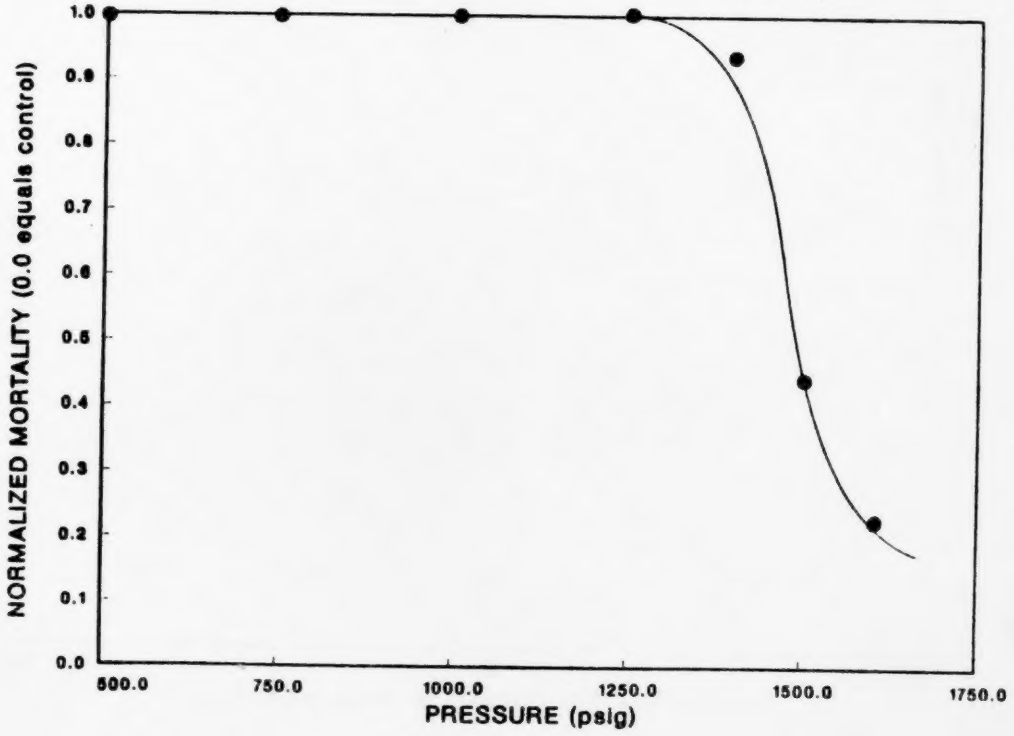


FIGURE 4. MORTALITY RESPONSE AS A FUNCTION OF PRESSURE



DURABILITY OF SLURRY CUT-OFF WALLS AROUND THE HAZARDOUS WASTE SITES

Raj P. Khera
Department of Civil & Environmental Engineering
New Jersey Institute of Technology
Newark, NJ 07102

Yuan H. Wu
Dames & Moore
6 Commerce Drive
Cranford, NJ 07016

M. Khalid Umer
Department of Civil & Environmental Engineering
New Jersey Institute of Technology
Newark, NJ 07102

ABSTRACT

This research was undertaken to study the long term behavior of a bentonite soil mixture interfacing with various chemical permeants. A chemically treated "contaminant resistant" Wyoming bentonite and a non-treated bentonite were tested. The tests show that the changes in the chemical concentrations have a measurable effect on the swelling index of the soil but the Atterberg limits were not affected by similar changes in concentrations. Long duration tests showed the swelling index for "contaminant resistant" bentonite to decrease with time whereas for non-treated ordinary bentonite its value stabilized in a much shorter period of time. For a given soil-chemical combination a straight line correlation was found to exist between swelling index and permeability.

INTRODUCTION

In recent years the use of slurry walls has increased as a containment structure for hazardous waste sites. However, there are little data supporting the long term effectiveness of slurry walls in controlling the migration of pollutants (2,4,5,9). Johnson, et al. (7) wrote,"... the technology regarding the use of slurry wall to contain hazardous wastes of all types is in its infancy ... further advancement is needed in developing tests of slurry wall materials to determine their long term performance."

Of all the engineering properties, the permeability of the backfill is the most important parameter affecting the performance of a slurry wall. However, the permeability tests are costly and very time consuming. Index properties tests such as Atterberg limit tests, though less expensive, are believed not to be reliable.

PURPOSE

The purpose of this investigation was to study the effect of chemicals of various concentrations on the long term behavior of slurry wall backfill materials. The usefulness of Atterberg limits as an index for determining the suitability of a backfill material was evaluated. Other properties, such as soil swelling which can be determined by performing simple tests, were investigated for the purpose of developing correlations between permeability and the swelling index defined later in this paper.

APPROACH

Soil Specimen

Two types of bentonites, an ordinary CS-200, a "contaminant resistant" SS-100 both supplied by the American Colloid Co., and a commercially available clean sand, were used for preparing backfill mixes.

Specimens for the swelling test were prepared by mixing 5ml of dry bentonite powder with various chemicals. To allow the soil particles and the liquid to interact freely, small quantities of soil and chemical were poured alternately in a graduate cylinder, to yield 100ml of uniform suspension.

To simulate the long term conditions, the test specimens were prepared by directly introducing chemical fluids of desired concentrations into the blended soils. The liquid contents for the backfill mixes were adjusted to approximately thirty percent to facilitate the molding of test specimens.

Equipment

Flexible wall and oedometer cells were used to determine the hydraulic conductivity (3). The triaxial cell and control panel were manufactured by Trautwein. Oedometers were of fixed-ring type, and sold by Soil Test.

In an oedometer, vertical stresses can be applied to simulate field overburden conditions, and the coefficient of permeability is obtained by indirect computations (6). The oedometer was modified to allow the direct measurement of permeability using the falling head technique.

Experimental Program

The impermeable nature of the bentonite is attributed to its unique swelling properties. When saturated with water, its volume expands 10 to 15 fold of its dry bulk (9). The volume change is governed by the nature of the fluid.

The swelling tests were conducted in essentially the same way as described by Head (6). The changes in the volume of soil suspension were recorded for several months.

To saturate a test specimen in the flexible wall permeameter, backpressure was applied in small increments and at a slow enough rate to prevent consolidation.

The premixed soil slurry was placed in the oedometer ring and was loaded to 25kPa. Direct measurements of hydraulic conductivity were made prior to each subsequent load increment.

The hydraulic conductivity for water was determined when the flow quantity versus the time curve became linear. For the chemical permeants the test was terminated when the rates of inflow and outflow became equal. Since the specimens were prepared by directly adding the chemical to the soil, the entire pore space was assumed to contain the chemical. Therefore, the waiting period for a two pore volume (2) displacement was considered unnecessary.

PROBLEMS ENCOUNTERED

The preparation of backfill mix required considerable time. The usual method to control its consistency through viscosity measurements (4,10) was abandoned in favor of controlling its liquid contents and slump.

The latex membranes, which are used to cover the test specimens in a flexible wall permeameter are readily attacked by the chemicals. To protect a membrane from the chemical attack the test specimen was wrapped two to three times with a teflon sheet. A thin coat of silicone grease was then applied to the teflon. The latex membrane was then placed over it.

For maintaining the shape of the specimen during mounting the application of a vacuum was ineffective due to the relative impervious nature of the backfill mix. A perforated sheet of aluminum foil wrapped around the sample outside the latex membrane provided the necessary lateral support for the specimen.

RESULTS

Atterberg Limits

The Atterberg limit tests were performed with toluene, aniline and phenol. The liquid limit with aniline dropped as the concentration increased. With phenol the liquid limit did not change even when the concentration was as high as 10,000 ppm. No correlation was observed to exist between the duration of soaking and the liquid limit. The data with toluene also showed a considerable spread. Thus, for the chemicals of the given concentrations, the liquid limit did not prove to be a useful index. Further Atterberg limit tests were curtailed in favor of swelling tests.

Swelling Tests

To correlate free swell with different chemicals a swelling index Si is defined as follows:

$$S_i = S_{wc}/S_{ww}$$

where S_{wc} is soil free swelling with a chemical and S_{ww} with demineralized water.

Initially the value of S_i for CS-200 was forty-five percent larger than that for SS-100. However, gradually the SS-100 specimens expanded and after twenty-five days S_i became constant and its final value was only fifteen percent less than that of CS-200.

Among the organic liquids aniline showed (Fig. 1) the most effect on S_i. With the concentration of 1,000 ppm and 10,000 ppm, the initial values of S_i were almost equal, but the 1,000 ppm suspension slowly increased its volume and became constant in about sixty days. For 10,000 ppm aniline, S_i continued to drop. This change became significant after four months and by the eighth month the difference between the two S_i values had increased from thirty percent to forty percent. Toluene and phenol also demonstrated some effect on S_i, though not as much as aniline. Similarly, Acar, et al. (1) reported greater reduction in free swell for concentrated aniline than for phenol.

Fig. 2 and Fig. 3 show the swelling indices for SS-100 with the highest chemical concentrations. The observation periods were almost twelve months for most of the chemicals. Note that the inorganic hydrochloric acid has the greatest effect on S_i. Also, potassium chromate has the lowest concentration but shows considerably more effect on S_i than other liquids with relatively higher concentrations. The higher charge on chromium ion is believed to have caused greater reduction in the thickness of the double layer and, therefore, lowered its swelling index. S_i for hydrochloric acid and chromium did not stabilized but for all other chemicals it became stable after two months.

Hydrochloric acid affected the swelling index of CS-200 (Fig. 4) to a greater extent than that of SS-100. However, for CS-200 the swelling index did not decrease with time as was the case with SS-100. Initially the S_i value for CS-200, was thirty percent lower than that for SS-100 but S_i decreased with time and in four months the difference between the S_i values for the two soils had reduced to less than five percent. The extrapolation of S_i for SS-100 shows it to be lower than that for CS-200. With the other chemicals, the S_i values for CS-200 were either equal to or greater than those for SS-100. Since SS-100 is chemically treated and is "contaminant resistant" one would expect its properties to be less affected by the chemicals. However, the observed results contradict the expected behavior.

The swelling index is more sensitive to the chemical type and its concentration and appears to be better suited for predicting the effect of chemicals on soils than the Atterberg limits. A swelling test is easier to perform and requires less skill than the Atterberg limit test, even though it takes longer to complete. Although the behavior of a soil suspension is not the same as its in-situ response, S_i can provide a qualitative measure of the influence of a permeant on the soil structure.

Hydraulic Conductivity

As shown in Fig. 5, with all other conditions remaining the same (void ratio, consolidation pressure, etc.), the swelling indices appear to show a linear relationship with the hydraulic conductivity for most of the chemical tested. The hydraulic conductivity increases as the swelling index decreases. These results are in agreement with the Gouy-Chapman theory which depicts the contraction of the diffused double layer primarily as the reason for the higher magnitude of permeability in a clay mass.

When using concentrated chemicals the change in permeability is usually dramatic and easily detected. At lower chemical concentrations the changes in the permeability are small and not detectable. The swelling index, on the other hand, is shown to be much more sensitive to small changes in the chemical concentrations. It is, therefore, a good indicator of a soils sensitivity to chemicals and the resulting changes in their properties.

The permeability values from oedometer and falling head measurements showed a good agreement and are presented elsewhere (8).

CONCLUSIONS

The use of the swelling index is a reasonable way for a qualitative evaluation of a soil-chemical interaction. The swelling index is much more sensitive to both the chemical type and its concentration. Long duration tests showed that the swelling index for "contaminant resistant" bentonite continued to decreased over a long period of time. However, for non-treated ordinary bentonite the swelling index stabilized in a much shorter period of time.

For a given soil-chemical combination a straight line correlation was found to exist between swelling index and permeability. As the swelling index of a soil decreases its permeability increases. This relationship can be used to predict the trends in soil permeability even at lower chemical concentrations.

ACKNOWLEDGEMENTS

This research was funded by the National Science Foundation Industry/University Center for Research in Hazardous and Toxic Substances, and the Department of Civil and Environmental Engineering, at the New Jersey Institute of Technology, Newark, NJ. Their support is greatfully acknowledged.

REFERENCES

1. Acar, Y. B., Hamidon, A., Field, S. D., and Scott, L.,"The Effect of Organic Fluids on Hydraulic Conductivity of Compacted Kaolinite," Hydraulic Barriers in Soil and Rock, ASTM, Johnson, A. I., Forbel, R. K., Cavalli, N. J., and Pettersson, C. B., Editors, 1985, pp. 171-177.

2. Anderson, D.,Crawley, W., and Zabcik, J. D.," Effect of Various Liquids on Clay Soil: Bentonite Slurry Mixtures,"Hydraulic Barriers in Soil and Rock, ASTM, Johnson, A. I., Forbel, R. K., Cavalli, N. J., and Pettersson, C. B., Editors, 1985, pp. 93-102.

3. Daniel, D. E., Anderson, D. C., and Boynton, S. S., "Fixed-Wall Versus Flexible-Wall Permeameters," Hydraulic Barriers in Soil and Rock, ASTM, Johnson, A. I., Forbel, R. K., Cavalli, N. J., and Pettersson, C. B., Editors, 1985,, pp. 107-126.

4. D'Appolonia, D.J.,"Soil Bentonite Slurry Trench Cutoffs,"Journal of Geotechnical Engineering Division, ASCE, Vol.106, No.GT4, April, 1980, pp. 399-419.

5. Evans, J. C., Fang, H. Y., and Witmer, K.,"Influenc of Inorganic Permeants upon the Permeability of Bentonite," Hydraulic Barriers in Soil and Rock, ASTM, Johnson, A. I., Forbel, R. K., Cavalli, N. J., and Pettersson, C. B., Editors, 1985, pp. 64-73.

6. Head, K. H., Manual of Soil Laboratory Testing, Vol. I and Vol. II, John Wiley & Sons, New York, 1981.

7. Johnson, A., Forbel, R. K., Cavalli, N. J., and Pettersson, C. B., "Overview," Hydraulic Barriers in Soil and Rock, ASTM, Johnson, A. I., Forbel, R. K., Cavalli, N. J., and Pettersson, C. B., Editors, 1985, pp. 1-6.

8. Khera, R. P., Wu, Y. H., and Umer, M. K.,"Durability of Slurry Cut-Off Walls around the Hazardous Waste Sites," Progress Report, NSF Industry/University Coperative Research Center, NJIT, Newark, NJ, 1986.

9. US EPA, "Slurry Trench Construction for Pollution Migration Control,"EPA-540/2-84-001, U. S. Environmental Protection Agency, Cincinnatti, OH, 1984.

10. Xanthakos, Petros P., Slurry Wall, McGraw-Hill Book Company, New York, 1979.

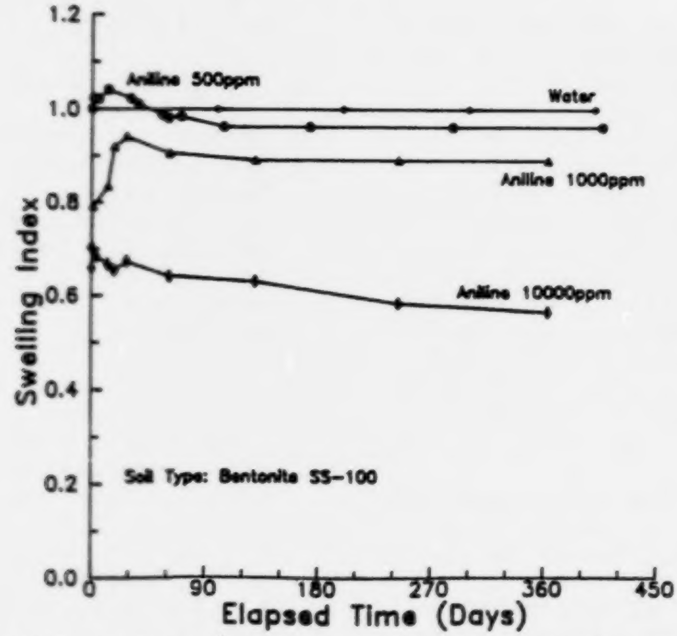


Fig. 1 Swelling Index of Chemically-Treated Bentonite, SS-100 with Aniline.

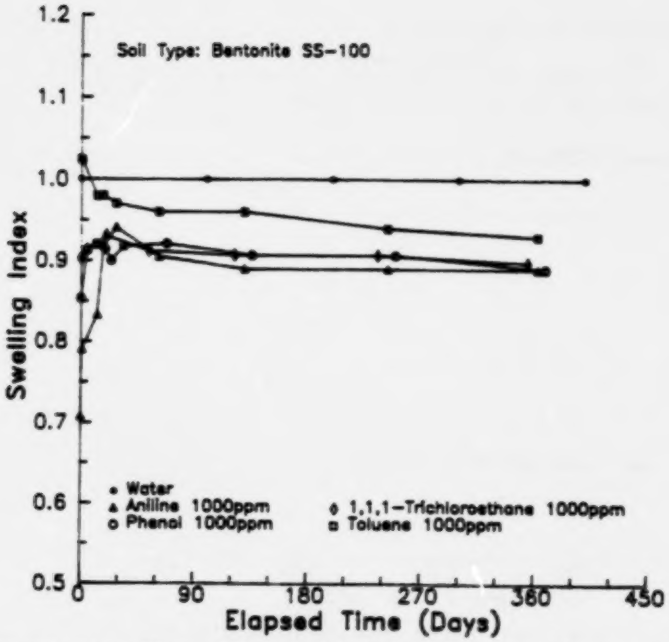


Fig. 2 Comparisons of Swelling Index for Chemically-Treated Bentonite, SS-100, with Organic Chemicals.

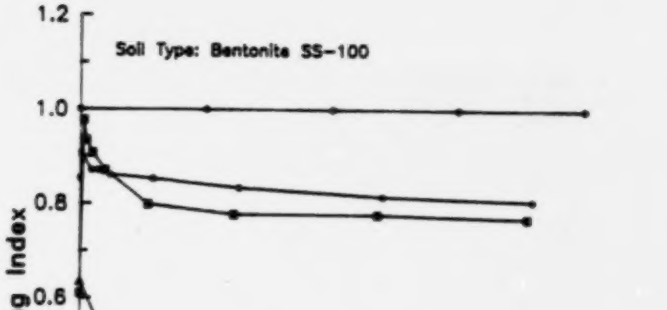


Fig. 3 Comparisons of Swelling Index for Chemically-Treated Bentonite, SS-100, with Inorganic Chemicals.

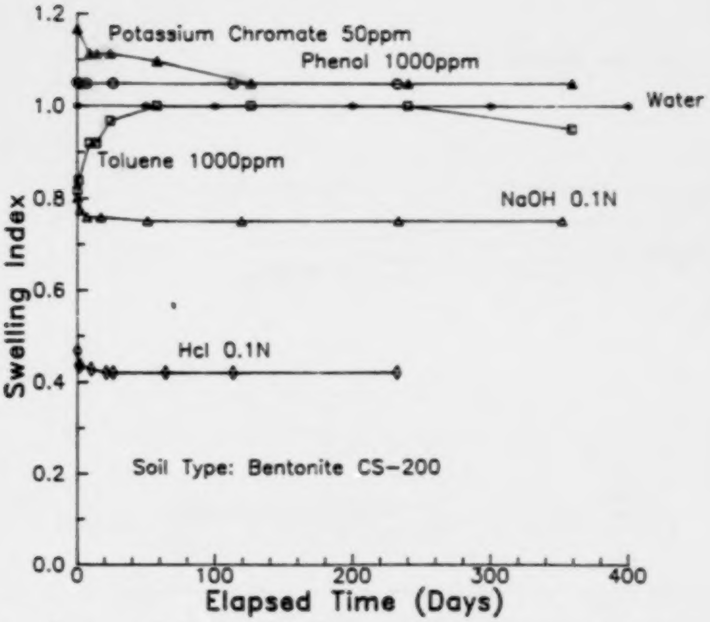


Fig. 4 Comparisons of Swelling Index for Ordinary Bentonite, CS-200.

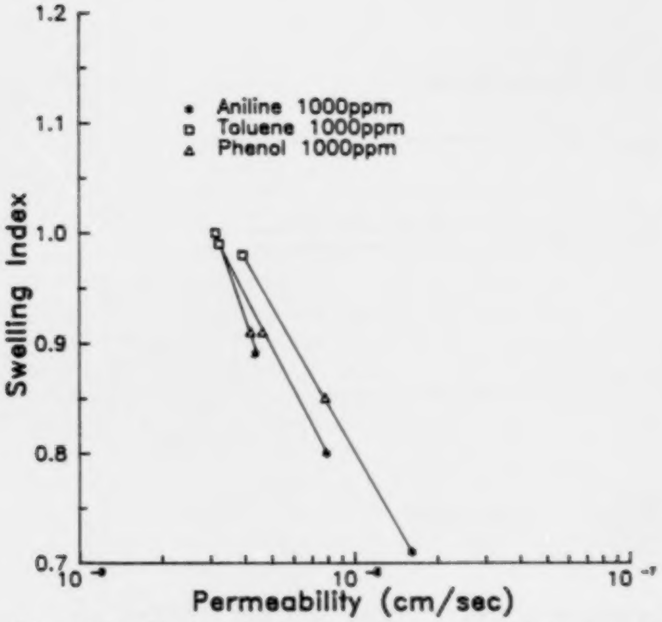


Fig. 5 Relationships between Swelling Index and Permeability for Backfill Mix with 10% Chemically-Treated Bentonite, SS-100.

Disclaimer

The work described in this paper was not funded by the U. S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

ASSESSMENT OF LEACHATE MONITORING AND TOXICITY IN GROUNDWATER AROUND IOWA MUNICIPAL LANDFILLS

Burton C. Kross, Ph.D., P.E.
Department of Civil and Environmental Engineering and
Department of Preventive Medicine and Environmental Health
University of Iowa
Iowa City, IA 52242

ABSTRACT

Historical monitoring data collected since 1977 at Iowa municipal landfills were analyzed to determine if groundwater was contaminated by landfill leachates. Monitoring data for indicator parameters - pH, chloride, and specific conductance - were examined statistically at 67 permitted municipal/county landfills using the student t-test and an analysis of covariance technique. Landfills were ranked into quartiles from greatest to least probability of contamination, based on historical data. A stratified random sample of 19 sites was then selected for further assessment using the Microtox toxicity screening procedure, chemical screening tests (TOC and TOX), and selected chemical analyses (ammonia, sulfate, nitrate, and heavy metals).

Results of toxicity and chemical screening procedures for groundwater from 93 wells at 19 landfills suggest a poor correlation between the two screening approaches. Wells that screened positive (12 total) for the TOX test were generally not the same wells that were considered toxic (10 total) according to the Microtox procedure. A significant correlation exits between Microtox and TOC data, as expressed by a Spearman rank correlation coefficient of 0.29 and a p-value of 0.006. Results of this study also suggest that TOC, ammonia, and sulfate are not good indicator parameters for monitoring leachate migration from landfills in Iowa.

The best approach to improving the quality of monitoring data around Iowa landfills is to increase the number and improve the location of new monitoring wells at each site. Commitment of financial resources in the future should be directed toward improved hydrogeologic representation of groundwater flow near landfills, not better chemical characterizations of groundwater quality.

INTRODUCTION

An important issue facing the nation is the protection of groundwater resources. An integral part of any protection strategy will be to define the extent, significance, and solutions to groundwater contamination from existing, identified, and unknown landfill sites. Initial investigations (1) of this issue by the Iowa Environmental Protection Division (formerly the Dept. of Water, Air, and Waste Management) focus on the 125 permitted landfills in the state, which utilize about 10,000 acres.

Review of existing records indicates that about 50% of these landfills are known to generate leachates. However, existing groundwater monitoring programs required at these landfills have detected leachate contamination of groundwater at less than 10% of the sites. This information may suggest one or more of the following scenarios.

a) that groundwater contamination from landfill leachates is not a problem,
b) that contamination is not yet a problem,
c) that contamination is not detected because of the insufficient number or location of monitoring wells,
d) that contamination is not detected because the most commonly required indicator parameters may not reliably indicate the presence of leachate contamination, or
e) the methods used to analyze existing monitoring data are not effective in determining contamination.

PURPOSE

Research was conducted to address scenarios c), d) and e) through investigating the relationship between toxicity of landfill leachates and other measured groundwater quality parameters. The objectives of this study were as follows:

1. Evaluate, analyze, and summarize existing monitoring data from all permitted municipal/county landfills in Iowa,

2. Conduct toxicity screening tests and limited chemical analyses on leachates and groundwater samples from chemical analyses on leachates and groundwater samples from 20 sites selected by stratified random sampling procedures,

3. Attempt to correlate results of the toxicity screening tests and chemical analyses with existing indicator screening tests and chemical analyses with existing indicator parameter data, and

4. Determine the applicability of a short-term bioassay screening procedure, the Microtox test (2), and several chemical indicator parameters for detecting leachate contamination of groundwater from landfills.

APPROACH

In an attempt to improve the homogeneity of field data, only municipal/county sanitary landfills (86 total) were considered for the database. Based on review of existing monitoring records, 19 landfills were deleted from further evaluation for various reasons, i.e. limited historical data from new monitoring well installations, only surface water monitoring at the site, or farm wells not properly constructed or located for monitoring purposes. The remaining landfills were then classified into two groups. Sites that included monitoring wells located up-gradient and down-gradient from the landfill were designated as Type I landfills (52 total). Type II sites (15 total) had monitoring wells in only down-gradient locations.

Historical monitoring data were available on a semiannual basis beginning in 1977-81 for most wells. Chemical indicator parameters, chloride, pH, specific conductance, and chemical oxygen demand (COD data for 1/4 of sites), were entered into the SAS, Version 5 (3) statistical assessment program for further analyses. The database includes 318 monitoring wells with about 10,000 observations.

Each monitoring well was classified as up-gradient or down-gradient. These designations were based on review of engineering and soils reports; potentiometric surface calculations performed using recorded water-level elevations, topographic elevations, and stratigraphic sequences for each monitoring well; and limited personal communications with agency staff.

The first level of statistical analyses used the standard T-test and a more sophisticated analysis of covariance (4) procedure for existing groundwater monitoring data for at all Type I landfills. The sites were then ranked and grouped into quartiles according to the calculated probabilities that a significant difference existed between up-gradient and down-gradient concentrations for the historical indicator parameters of chloride and specific conductance.

A stratified random sample was constructed by randomly selecting 6 sites from the first quartile (greatest probability of contamination), 5 sites from the second quartile, 3 sites from the third quartile, 3 sites from the fourth quartile, and 3 Type II sites. This technique permits calculation of an inclusion probability for use in weighted regression analysis. Hence, the method preserves the statistical validity of this study for drawing inferences about potential groundwater contamination from landfills throughout Iowa.

At each of the 20 selected landfills, samples of groundwater from existing monitoring wells were collected using standardized field procedures. Measurement of pH, specific conductance, chloride, ammonia nitrogen, nitrate, and sulfate was performed using a portable spectrophotometer (Hach Model DR/3). Samples were analyzed for total organic carbon (TOC) and total organic halides (TOX) by the University Hygienics Laboratory. At three sites, analyses for 11 heavy metals and 28 volatile organics were performed on 24 environmental samples, including landfill leachates.

The Microtox single point screening methodology for 100% samples was used for the groundwater samples. Responses for three replicate samples from each well were compared to the response of three diluent blanks. Sample pH was adjusted to 6.0 to 7.0. Testing temperature was 10°C. This procedure produced a response that was expressed as a positive or negative percentage of light reduction. A positive light reduction suggests a toxic response while a negative light reduction indicates stimulation or possibly hormesis (5).

The Microtox test is based on detecting changes in natural light production from a specific strain of a marine luminescent bacterium, Photobacterium phosphoreum, when exposed to a toxic challenge. The bacteria are carefully cultured and harvested to insure genetic stability and are provided by the manufacturer in lyophilized form. Each test involves about 3 million of the reconstituted bacteria (30 ul. per

1.0 ml. sample). The Microtox Model 2055 Toxicity Analyzer System used for this procedure contains a spectrophotometer that measures the differences in light output of samples compared to light output of diluent blanks. Light measurements were recorded 5 and 15 minutes following inoculation of the sample with bacteria.

Results of toxicity testing and chemical analyses for 93 wells at 19 landfills (one landfill declined participation) were analyzed using SAS correlation and regression procedures.

PROBLEMS ENCOUNTERED

Despite careful use of existing records and historical hydrogeological observations, field investigations at the 19 landfills detected probable discrepancies in previous designations of monitoring wells as up-gradient or down-gradient. Nine wells were reclassified based on field verification and a third classification "within the fill" was created for six wells that were actually monitoring groundwater in or near old landfill waste cells. It is important to recognize that field verification of monitoring data is essential. Changes for 15 of 93 wells resulted in reordering and significantly different statistical inferences at 8 of the 19 landfills.

Field observations were also important relative to assessing the effectiveness of each existing monitoring network. At 8 of the 19 sites, additional wells would be required to establish a minimal basis for monitoring groundwater movement around the site. The most common deficiency was the lack of good up-gradient locations to serve as a baseline. Another monitoring problem occurs when landfilled areas become local recharge zones, thereby changing the local groundwater flow direction as the landfilling progresses.

The standard Microtox test procedure necessarily involves dilution of the sample to about 70% of its original concentration; followed by serial dilutions at even lower concentrations to obtain data for a log-log plot of concentration vs. normalized light production. For many of the groundwater samples this standard Microtox procedure at 15°C resulted in "negative" data points or stimulation of the bacteria at the lower concentrations. Perhaps nutrients in the sample produced true stimulation of the bacteria or perhaps hormesis from low levels of toxicants was the cause of these observations. In any event, it was not possible to calculate the normal Microtox toxicity endpoint, i.e., the EC20 or EC50, for most of the samples. Better results for toxicity screening purposes were obtained using the Microtox single point screening methodology for 100% samples.

RESULTS

The preliminary statistical analyses of 52 Type I landfills determined that 13 sites historically had significantly higher (p-value <0.05) concentrations for chloride in down-gradient wells vs. up-gradient wells. Similarly, 16 landfills had the same condition for historical specific conductance measurements. A total of 7 landfills had significant differences in historical records for both indicator parameters. From a research viewpoint this ranking of sites was useful to assure that field testing encompassed the full range of expected groundwater contamination around landfills during the limited field study. The environmental policy and regulatory significance of these rankings are of obvious importance, as well.

Validation tests on metal solutions and diluted landfill leachates were performed to determine the sensitivity of the Microtox single point screening method. Reference standards containing known concentrations of metals regulated by the Safe Drinking Water Act were analyzed. Based on the results given in Table 1, the Microtox method appears to be sensitive enough to detect small amounts of leachate in groundwater. Additional chemical analyses for leachates from two sites are given in Table 2.

Summary data for the Microtox tests and other chemical parameters measured at 93 wells monitoring 19

Table 1. Calibration Data

Compound	Conc. mg/L	Microtox NPLD-5 min	 NPLD-15 min
Arsenic	0.05	14.1	17.5
	0.5	21.5	36.2
Silver	0.05	25.6	28.0
	0.5	24.1	65.2
Lead	0.05	16.1	19.4
	0.5	22.5	41.6
Selenium	0.01	14.1	14.4
	0.1	11.7	16.0
Cadmium	0.01	5.2	8.1
	0.1	1.1	5.0
Mercury	0.002	15.1	17.9
	0.02	4.3	9.4
Chromium	0.05	4.3	6.6
	0.5	4.3	6.8
Barium	1.0	0.7	4.2
	10	0.0	6.3
Chlorine, w/Ammonia	0.1 5.0	40.5	172.
Chlorine, w/Ammonia	1.0 5.0	327.	--
Millipore Water		3.1	11.8
Water Leachates			
Leachate A	400:1	2.4	3.6
	20:1	89.6	84.0
Leachate B	400:1	11.2	28.0
	20:1	161.	194.
Leachate C	400:1	-1.3	-0.5
	20:1	23.8	21.0
Leachate D	400:1	8.7	14.0
	20:1	404.	770.

Notes: NPLD = net % light decrease, 10°C.
Lowest conc. of metals is drinking water standard

Table 2. Analyses of Landfill Leachates

Parameter	Site A	Site B	Parameter	Site A	Site B
Tox (PPB)	320	910	Mg (PPM)	260	300
TOC (PPM)	610	2500	Se (PPM)	0.01	< .01
Ba (PPM)	.16	1.2	Zn (PPM)	0.78	0.58
Cr (PPM)	< .02	0.36	Cu (PPM)	0.06	< .05
As (PPM)	0.03	< .01(PPM)	Ag (PPM)	< .01	< .01
Cd (PPM)	0.02	0.02	Trichloro-floromethane (PPB)	1414	< 5
Pb (PPM)	0.13	0.19(PPM)			

Table 3. Summary Results of Toxicity and Chemical Testing

Test	Mean	S.D.	Range Low	Range High
NPLD5	5.1	13.5	-15	77
NPLD15	-5.6	42.5	-27	386
TOC	14.1	31.2	.5	200
TOX	58.4	94.0	5	540
NH3, N	0.5	0.6	0	3.5
NO3, N	1.2	2.6	0	16
SO4	97	150	0	785
pH	7.1	0.3	6.0	8.2
Sp. Cond.	1110	760	300	5200
Cloride	23.3	65	1	460
Del. Cloride	15.6	84	-76	593
Del. Sp. Cond.	130	470	-480	1750

Note: Microtox tests 10°C. All concentrations in mg/L, except TOX in PPB. Del. = delta, down-gradient minus up-gradient

Table 4. Microtox Data Classification System

NPLD-5	Classification	# of wells
> 32	very toxic	5
18 - 32	toxic	7
10 - 18	slightly toxic	8
0 - 10	indeterminate	40
< 0	non-toxic	33

Table 5. TOX Screening Classification System

TOX	Classification	# of wells
>178	strong positive	6
100-178	positive	6
56-100	weak positive	7
32- 56	indeterminate	23
< 32	negative	49

landfills are presented in Table 3. Results from any toxicity screening procedure should not be considered absolute measurements of toxicity. A classification scheme for grouping Microtox results into a ranking system is suggested in Table 4. Similarly, chemical screening tests like TOX could be grouped into classifications that indicate the need for additional specific chemical analyses. See Table 5. These rankings are based on increments of 0.25 on a log 10 scale. For example, wells that were classified as very toxic/toxic by the Microtox test or strong positive/positive by the TOX test could be analyzed for heavy metals, specific volatile organics, or other suspected contaminants.

Microtox and chemical analyses data are very skewed data sets with several observations beyond three standard deviations from the mean. These observations were deleted for statistical analyses using non-parametric methods. The correlation between Microtox and TOX data is not significant, resulting in a Spearman rank correlation coefficient of 0.15 with a p-value of 0.15. Stated another way, the wells that screened strong positive/positive for the TOX test usually were not the same wells that were very toxic/toxic based on the Microtox procedure. This result is not surprising since Microtox procedures can detect a much broader range of toxicants in groundwater than TOX measurements. Moreover, Microtox is not particularly sensitive to low concentrations of halogenated organics.

A significant correlation exists between Microtox and TOC data, with a Spearman rank correlation coefficient of 0.29 and a p-value of 0.006. This correlation between total organic carbon and Microtox toxicity is consistent with the broad screening nature of both procedures.

An analysis of the 13 study sites, which have up- and down-gradient wells (76 total), using the inclusion probability method yields statistical inferences about likely monitoring results for all landfill monitoring wells in Iowa. The data presented in Table 6 represents the best estimate, based on this stratified random sample of 13 sites, of expected values for chemical parameters and toxicity in groundwater near Iowa landfills.

Highly significant differences (p-values <0.01) exist between up-gradient and down-gradient observations for the Microtox procedure, TOX, specific conductance, and chloride. Of particular note, measurements of TOC were essentially the same for up and down locations while up-gradient measurements of sulfate, and ammonia were actually higher than down-gradient observations. These data suggest that TOC, sulfate, and ammonia testing are of limited utility for monitoring potential landfill contamination.

RECOMMENDATIONS

1. The computerized database for existing landfill monitoring networks should be maintained and updated with semi-annual data by the Iowa Environmental Protection Division. Designations of wells as either up- or down-gradient should be carefully reviewed for all sites by regionally based state inspectors who regularly visit each landfill.

2. The best approach to improving the quality of monitoring data is to increase the number and improve the location of new monitoring wells at each landfill.

3. Given the inherent limitations of the existing monitoring database, the simple student t-test procedure is

Table 6. Best Estimate for Statewide Monitoring Results

	Up-gradient (n=19)			Down-gradient (n=57)			Student
		Range					t-test
Parameter	mean	low	high	mean	low	high	p-value
Microtox							
NPLD5	2.0	-7.8	23.4	3.8	-14.9	45.8	.0085
TOX	40	5.0	160	62	5.0	540	.0001
TOC	7.8	.5	68	8.5	1.0	150	.6060
Sp. Cond.	870	415	1880	1080	300	3550	.0003
Chloride	5.2	1.0	99	20.5	1.0	460	.0001
Sulfate	92	10	700	88	0	785	-.0281
Nitrate, N	1.8	0	8.3	0.9	0	12	-.0060
Ammonia, N	0.6	0	3.1	0.4	0	1.5	-.0301

appropriate for determining the significance of differences between up-gradient and down-gradient wells. Student t-tests should be performed in conjunction with each monitoring period. Examining data from individual wells alone with actions taken if single observations deviate from the mean by more than 3 standard deviations will not effectively utilize the monitoring database.

4. Two baseline monitoring wells carefully located in up-gradient locations that will not be disturbed by on-going landfilling operations should be required at each landfill. If the landfill could affect the groundwater table and additional aquifers, two baseline monitoring wells should be placed in each groundwater regime. These wells may necessarily be located off landfill property to insure constant baseline data.

5. At the time of permit renewal, each landfill operation should submit results of a detailed hydrogeology report based on site-specific field testing to justify the number and location of on-going groundwater monitoring wells.

6. A recording rain gauge, field measurements of infiltration rates into the landfill cap, and field estimates of evapotransporation rates over the landfill area should be added as permit requirements to assist with water balance calculations needed to predict leachate generation rates.

7. Each landfill should establish a surface water monitoring program to include upstream and downstream samples of intermittent drainage ditches, ponding water, or streams draining the site. If local groundwater flows are known to contribute to streamflow in the immediate vicinity of the landfill, sampling of the stream should also monitor this condition.

8. Sampling of farm wells in the vicinity of landfills may have public relations benefits (assuming all results are negative), but these samples have little monitoring benefit because of inconsistent well construction and significant potential for other interference contamination, i.e. feedlot or agricultural chemical spills. Farm wells should be deleted from future monitoring requirements.

9. On-site wells used for potable water supply by landfill workers should be added to the monitoring

requirements. Testing requirements should parallel those required for small public water systems under the Safe Drinking Water Act.

10. Although current indicator parameters (chloride, pH, and specific conductance) are probably not the best approach to consistently detect groundwater contamination from landfills, extreme caution should be exercised before adding new chemical parameters to monitoring requirements. Any additions should have a specific rationale and stated interpretation guidelines. As previously noted in no. 2 above, financial resources should be directed toward improved hydrogeologic representation, not chemical characterizations.

11. Further assessment of screening procedures like TOX and Microtox may ultimately lead to inclusion of one or more of these tests to a complete groundwater monitoring program.

ACKNOWLEDGEMENTS

The financial and technical support of the U.S. Environmental Protection Agency and the Iowa Division of Environmental Protection is greatly appreciated. Analytical support and equipment for toxicity measurements were provided by the University Hygienic Laboratory and Microbics Corporation. Special thanks go to Barbara Torney, a geologist, who assisted with interpretation of hydrogeological data.

REFERENCES

1. Beckman Instruments Inc., 1982, Microtox System Operating Manual, Carlsbad, CA, 94 p.

2. Hoyer, B.E., J.E. Combs, R.D. Kelley, C.C. Leatherman and J.H. Seyb, 1987, Iowa Groundwater Protection Strategy, Environmental Commission, Des Moines, IA, 106 p.

3. SAS Institute Inc., 1985, SAS User's Guide: Basics, Version 5 Edition, Cary, NC, 1290 p.

4. Silver, C.A., 1985, Statistical Approaches to Groundwater Monitoring, Environmental Institute of Waste Management Studies, University, Alabama, 18 p.

5. Stebbin, A.R.D., 1982, Hormesis - the stimulation of growth by low levels of inhibitors, In: The science of the Total Environment, Elsevier Scientific Publishing Co., Amsterdam, Netherlands, pp 213-234.

DISCLAIMER

The work described in this paper was not funded in total by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

LEACHATE SYNTHESIS FOR CLAY
AND
FML COMPATIBILITY TESTING

Stephen S. Odojewski
Waste Resource Associates, Inc.
2576 Seneca Avenue
Niagara Falls, NY 14305

ABSTRACT

In complying with permitting requirements for land disposal facilities, a new facility faces certain problems not encountered by an existing facility. In particular, the required demonstration of the compatibility of the liner system with the wastes and associated constituents to be handled becomes much more complicated. A logical approach can however be employed to formulate a synthesized leachate which can then be used to produce the data needed to satisfy the requirements of this demonstration.

In this particular project, the leachate which was synthesized was shown to be compatible with both a FML of high density polyethylene (HDPE) and a clayey soil liner.

INTRODUCTION

As part of the permitting process for any existing or new land disposal facilities in the United States, the permit applicant must demonstrate that the various materials chosen for the liner system are compatible with the hazardous wastes and associated constituents to be disposed. In the case of an existing facility, the compatibility demonstration usually involves obtaining a representative sample of leachate generated from on-going land disposal operations and subjecting the various components of the liner system to the appropriate compatibility testing protocols. Since a new facility cannot begin to accept any hazardous wastes for disposal until a permit is issued, the compatibility demonstration becomes a somewhat more complicated undertaking. The new facility permit applicant is forced to somehow synthesize a leachate which is representative of the types of wastes intended to be disposed at the facility. This leachate must then be used to perform the required compatibility testing.

Preceding page blank

PURPOSE

Whatever approach is used to formulate the synthesized leachate must be technically defensible with respect to ensuring the leachate is representative of future land disposal activity. As certain assumptions are made in developing the approach, the permit applicant must be sure to employ a "worse case" scenario. This is particularly important when selecting the range of waste constituents to be included in the synthesized leachate as well as the concentrations in which they must be added. Only with a synthesized leachate representative of future land disposal operations (or a more highly contaminated leachate) can the compatibility of the materials of construction selected for the proposed liner system be verified.

APPROACH

The first step in formulating a synthesized leachate involved determining which waste types the proposed facility intends to handle. Part 261 of Title 40 in the U.S. Code of Federal Regulations presents the methodology by which a waste generator determines if his waste is "hazardous." There are two basic mechanisms by which a waste can qualify as "hazardous"; inclusion in any one of four "lists" presented in Subpart D of Part 261 or meeting any one of four "characteristics" presented in Subpart C of Part 261. In reviewing each of the waste types described in Part 261, the permit applicant must decide whether any exclusionary land disposal restrictions such as physical form (i.e. liquid or presence of free liquid) or unique hazards (i.e. highly reactive, extremely low flash point) will prevent the proposed facility from accepting that waste. It should be noted that many of the EPA wastes listed in Subpart D, might initially be thought to be excluded from consideration because they are liquids may, in fact, be accepted by the facility because of the mixture rule of 40 CFR 261.3 or because they are residues derived from the treatment of a particular Subpart D listed waste. Examples are spill residues (soil) contaminated with a liquid commercial chemical product or the solidified form of a semisolid waste.

For each of the Subpart D wastes which the facility intends on handling, Appendix VII to Part 261 lists the major hazardous constituents the EPA expects to be present in that waste. The constituents listed in Appendix VII that are contained in the various listed wastes to be handled by the facility formed the initial basis for determining which chemical compounds were to be contained in the synthesized leachate. This initial list was further expanded after a review of the hazardous constituents presented in Appendix VIII to Part 261. Appendix VIII constituents which have a flash point less than 140°F or which may be present as minor waste constituents were then added to the initial list of chemical compounds to ensure it was as complete as possible.

The permit applicant then estimated the annual volume for each of the various waste types that the facility intends on accepting. These estimates were based on the type and number of generating industries located within the intended service area of the facility. The annual volume estimates were then sub-divided and placed into either "low", "medium" or "high" receipt volume categories.

A concentration was then assigned to each constituent which was to be included in the synthesized leachate as a result of the review of Appendix VII and Appendix VIII. This concentration was established based on the number of wastes which contained that chemical compound and the relative volume of these wastes with respect to the annual volume of all wastes which are expected to be received.

Once the completed list of constituents and their corresponding concentrations had been compiled, the appropriate material for the FML was chosen. Existing manufacturer compatibility data for each of the pure chemical compounds contained in the synthesized leachate was examined and the FML which offered the widest range of chemical resistance was chosen.

In a new facility which intends on accepting a relatively wide variety of different waste types, it is not uncommon to develop a lengthy listing of constituents which must be combined in order to properly synthesize the leachate to be used for testing. Such was the result of this effort. The listing may contain many chemical compounds which are either insoluble in water or have limited solubilities (i.e. chlorinated hydrocarbons). In order to attempt to dissolve as many of the water-insoluble substances in the synthesized leachate, it was helpful to prioritize or rank the chemical compounds with regard to their water miscibility or solubility. Four categories for the prioritization or ranking were established. These categories included compounds which are either;

- completely miscible with water in all proportions,
- water soluble but not completely miscible in all proportions,
- limited water solubility
- insoluble (negligible solubility in water).

The chemical compounds which fall into the first category were initially added to the distilled water used as the base for synthesizing the leachate. These were followed by those in the second category and so on. By using this sequence of addition, it is more likely that some of the compounds with either limited or negligible solubilities in water (but which may be soluble in certain organics) were actually "pulled into" solution and dissolved into the synthesized leachate.

PROBLEMS ENCOUNTERED

As the laboratory responsible for actually formulating (mixing) the synthesized leachate began contacting various chemical supply vendors, certain chemical compounds could not be obtained. Some examples of Appendix VIII hazardous constituents which were found to be commercially unavailable are:

- Dichlorophenylarsine
- Diethylarsine

- alpha, alpha-Dimethylbenzylhydroperoxide
- Lead phosphate
- Nickel carbonyl
- symmetrical-Trinitrobenzene

Certain chemical compounds which were deleted from the list because they were too volatile to be expected in any appreciable concentration level in the uncontainerized wastes handled by the facility and too volatile to be effectively dissolved into the synthesized leachate. Examples of these highly volatile compounds are:

- Carbon disulfide
- 1,1-Dichloroethane
- Ethylene oxide
- Vinyl chloride

Other chemical compounds were found to be unstable when introduced into an aqueous matrix and therefore deleted from the synthesized leachate. Examples of these compounds are:

- Antimony compounds
- Methyl isobutyl ketone peroxide
- Phosphorous sulfide
- Toluene diisocyanate

In order to enhance the solubility of certain inorganic metallic chemical species in the leachate, the chloride salt of various inorganic metallics was chosen in lieu of other chemical forms with lesser water solubilities.

RESULTS

Upon completing the addition of all chemical compounds which could be obtained commercially, 15.0 liters of leachate was produced. The synthesized leachate separated into three distinct phases (or layers). These phases, from top to bottom, were:

- 8.0 liters of a clear, yellow-green liquid;
- 4.5 liters of a flocculant precipitate;
- 2.5 liters of a heavy sludge.

Since the minimum technology guidelines issued by EPA for double liner systems for landfill facilities requires that an upper FML be overlain with a primary leachate collection zone designed to prevent clogging, only the clear, yellow-green liquid was used in the ensuing compatibility testing. A well-designed primary leachate collection zone will prevent any of the flocculant precipitate and/or heavy sludge from penetrating down into the zone and blinding its hydraulic transmission capabilities. Therefore, the only phase from the synthesized leachate likely to penetrate the entire thickness of the primary leachate collection zone and contact the primary FML would be the clear, yellow-green liquid.

In order to confirm precisely which of the chemical compounds originally added to the synthesized leachate blend did in fact remain in the upper liquid phase, the clear, yellow-green liquid was analyzed. Nearly all of the inorganic (metallic) chemical compounds added to the leachate remained in varying degrees in the upper aqueous layer while approximately only 20% of the organics added were detected. The table which follows lists the various inorganics and organics, the concentrations in which they were added to the leachate and the concentration for that constituent found in the upper aqueous layer.

Synthesized Leachate Analysis

pH = 2.7
specific gravity = 1.12
conductivity = 185,000

TOC = 5,000 mg/l

organics:	(mg/l)
phenol	130
2-picoline	130
2-chlorophenol	56
1,2-dichloroethane	55
methylene chloride	43
nitrobenzene	32
cyclohexanone	25
aniline	21
nitrophenol	20
chloroform	18
1,1,2-trichloroethane	17
p-chloro,m-cresol	14
MIBK	12
nitropropane	12
propanenitrile	12
2-methyl phenol	12
pyridine	10
dichlorophenol	9.1
dinitrotoluene	8.5
methyl chloroform	8.0
trichlorophenol	7.1
acetone	7.0
acrylonitrile	6.5
ethyl acrylate	6.2
dinitrobenzene	5.7
1,1-dichloroethane	5.6
benzyl alcohol	4.3
butanol	2.5
benzene	2.3
3-chloro,2-butanone	1.8
trichloropropane	1.5
chlorobenzene	0.5

inorganics (anions):	(mg/l)
chloride	43,000
sulfate	34,000
nitrate	10,000

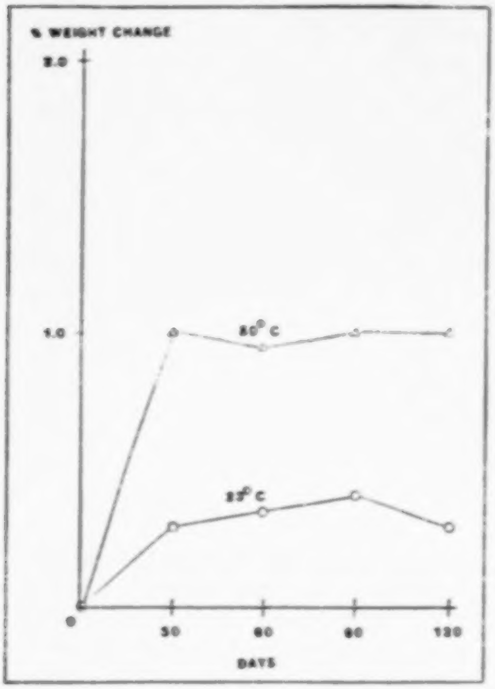
inorganics (cations):	(mg/l)
sodium	34,000
potassium	12,400
aluminum	4,100
magnesium	3,680
copper	2,130
zinc	1,310
boron	1,200
cadmium	1,020
lithium	640
bismuth	<500
lead	392
manganese	367
nickel	268
selenium	202
strontium	180
mercury	110
arsenic	106
antimony	53.3
cobalt	43.3
calcium	34.8
molybdenum	28.5
phosphorus	22.0
tin	15.4
iron	9.3
thallium	6.1
beryllium	1.6
vanadium	1.3
silver	0.22
barium	0.13

There were many organics which were added to the synthesized leachate that were not identified in the analysis of the upper aqueous layer. It is felt that these organics were either reacted in some way to form the insoluble precipitate or sludge or volatilized.

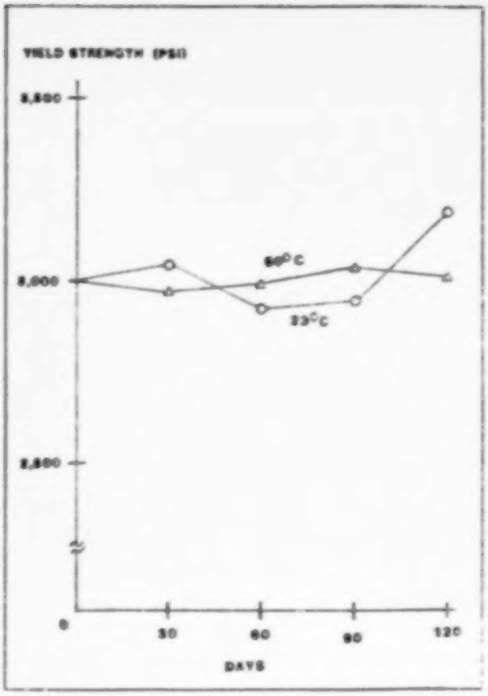
The clear, yellow-green liquid was used to subject a high density polyethylene FML to compatibility testing using EPA Method 9090 and a sample of clayey soil material to compatibility testing using EPA Method 9100.

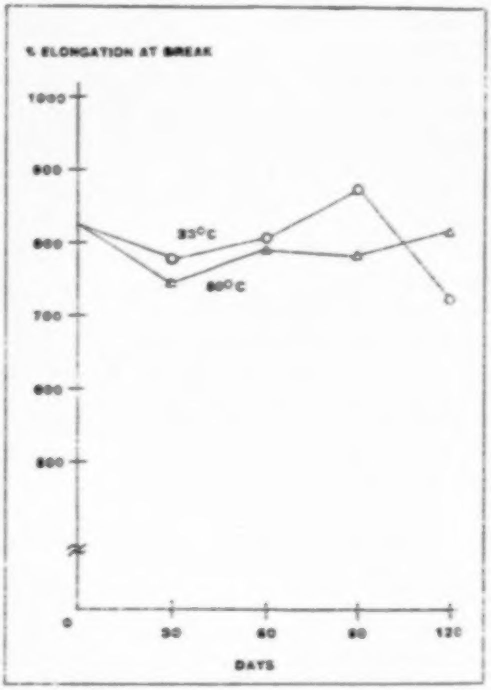
HDPE Testing

The three figures which follow detail the testing data for percent weight change, yield strength and percent elongation at break for the high density polyethylene FML subjected to Method 9090 compatibility testing.



No significant deterioration of the high density polyethylene FML was identified in the Method 9090 testing which was conducted.





Clay Testing

The recompacted permeability of a clayey soil sample was determined by ASTM Method 2434 using both deionized water and the synthesized leachate as a permeant. The results of that testing is as follows:

Permeant	% Moisture	k (cm/sec)
Deionized Water	13.9	3.99×10^{-8}
Synthesized Leachate:		
Trial No. 1	13.6	2.60×10^{-8}
Trial No. 2	14.2	2.45×10^{-8}
Average	13.9	2.53×10^{-8}

The synthesized leachate had no discernable effect in deteriorating or altering the permeability of the clayey soil.

ACKNOWLEDGEMENTS

This project was conducted on behalf of our client, Sechan Limestone Industries, Inc. (Portersville, PA), who graciously agreed to share this information.

The blending of the synthesized leachate, analysis for inorganic constituents and the clayey soil testing was conducted by the Calspan Advanced Technology Center (Buffalo, NY).

The analysis for organic constituents was conducted jointly by Advanced Environmental Systems, Inc. (Niagara Falls, NY) and Compu Chem Laboratories (Research Triangle Park, NC).

The testing of the HDPE liner was conducted by Gundle Lining Systems, Inc. (Houston, TX).

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

MINIMIZATION OF WASTE UTILIZING HIGH PRESSURE MEMBRANE FILTER PRESSES

C. Robert Steward, P.E.
Shriver Filter Presses/Eimco Process Equipment Company
1476 Montgomery Highway
Birmingham, AL 35216

ABSTRACT

Presentation to discuss the technology used in high pressure filtration utilizing variable volume membrane filter plates to produce the highest dry solids and minimal volume of liquid waste when dewatering a hazardous waste slurry. Presentation will address effects of pressure, conditioning, operation of membrane (diaphragm) plates, and areas to consider in the design of an installation.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

****

WHERE ENTIRE PAPER HAS NOT BEEN INCLUDED IN THESE PROCEEDINGS COPIES WILL BE AVAILABLE IN THE CONFERENCE LOBBY.

Preceding page blank

SOIL STANDARDS FOR HAZARDOUS WASTE DISPOSAL AND CLEANUP IN THE NETHERLANDS

F. B. DeWalle
TNO, Delft, 2600 AD, Holland
University of Washington, Seattle, WA 98195, U.S.A.

ABSTRACT

The present study established reference values for uncontaminated soils in relation to clay content and organic matter. These reference values are to be used to designate soils that are contaminated by hazardous waste and releases from point sources. The limited dose-effect relationships for the different soil functions indicate levels comparable to the reference values. Soil remediation techniques were generally not able to reach these reference values and disposal of cleaned-up soil therefore still requires usage restrictions.

INTRODUCTION

The Netherlands is a densly populated country with 15 million inhabitants occupying 41,160 km^2. Many conflicting demands are placed on soil use. More than 2 billion m^3 groundwater are annually withdrawn (influencing 14% of the land area) and 125 million m^3 sand and clay are used for building materials each year. A large part of the annual 5 million tons domestic refuse and 20 million tons industrial waste is disposed of on the soil. In addition, 12 tons cadmium, 400 tons lead and 1600 tons zinc are added to the soil through wet deposition from the air. More than 7500 contaminated locations, covering an estimated 20% of the total soil area have been identified of which more than 1600 need remedial action (VROM,1987; Nypels, 1986).

The urban areas, covering 7.6% of the land, contribute to soil pollution through leaking sewers , corroded tanks and infiltrating urban runoff. The soil usage for roads (1.8% of the land) contribute as a result of contaminated runoff, spills and deposition from the air. The agricultural areas (64.5% of land use) receive large quantities of fertilizer, sewage sludge and pesticides. Even the unused natural areas and and forests (covering12.1% of the land) and water (covering 9.0% of the land) are subject to degradation through upwelling contaminated groundwater, deposition from the air and polluted sediments (Biemond, 1978).

SOIL PROTECTION POLICY

Soil protection has received considerable attention in the Netherlands. The Interim Soil Cleanup Act covering the period 1982-1988 deals primarily with remedial action of locally contaminated areas and dump sites that pose a harmful effect to human health or the environment.

The Soil Protection Bill which was first submitted to parlement in 1980 became law on January 1, 1987. It is the intention of the Act that soil use does not diminish its multifunctionality, i.e., its agricultural function (crop production and grazing), groundwater recovery function, ecological function, mining function and carrier function, primarily through prevention measures. The Act provides for a general level of protection through soil quality standards and goals and source reduction. It allows for additional protection in watersheds

Preceding page blank

or groundwater protection areas and soil protection areas (unique natural habitats, rare soil strata or archeological sites). The soil quality standards can deal with physical (mechanical degradation), biological and chemical aspects of the soil and are to be specified in subsequent rules and regulations (article 20). A policy distinction is made between chemicals that are harmfull and cause irreversible damage that must be prevented from coming into contact with the soil whenever possible (black list) and those that may be deposited on the soil providing strict requirements are met (grey list). Point sources are covered by ICM (isolate, control, monitor) criteria, while input from the diffuse sources (deposition from air, heavy metals in fertilizer, sewage sludges, etc.) should equal output (leaching, crop removal).

The first soil criteria established in 1983 under the Soil Clean-up Act were based on a) nature and concentration of the pollutant; b) local situation through site specific risk analysis in which an individual risk of 10^{-6}/year per substance is maximum tolerable and 10^{-8} is negligible; and c) use and function of the soil and restoration of its multifunctionality. It contains "A" or reference values below which a "good" soil quality exists, "B" values below which a preliminary investigation is likely because of uncertainty regarding good soil quality and "C" values below which possible harmfull effects for human health or the environment can occur requiring further investigation and above which the soil is heavily polluted requiring remedial investigations and cleanup preferrably back to the "A" value. These indicative A,B,C- concentration values for both soil and groundwater are shown in Figure 1. The values for group 1 and 2 components present average background concentrations while the values for group 3 through 7 represent analytical detection limits. The EC directive for drinking water standards apply for deep groundwater and for drinking water (EC, 1980). The major shortcoming of the values were the limited toxicological basis and past experience on which they were based, the inability to differentiate according to soil type and the absence of criteria for radioactive substances and bacterial contaminants (Moen et al., 1968). In April, 1986, the Ministry of Housing, Physical Planning and Environment (VROM, 1986) proposed "tentative reference values" for a good soil quality that met the multifunctionality criterium. The proposal was submitted to the Technical Soil Commission (TCB) appointed by the Minister, to advise on the technical and scientific merits of the proposal. The material presented below was the basis for the TCB advice. It was developed by six task forces with a total of 43 academic participants (TCB, 1986).

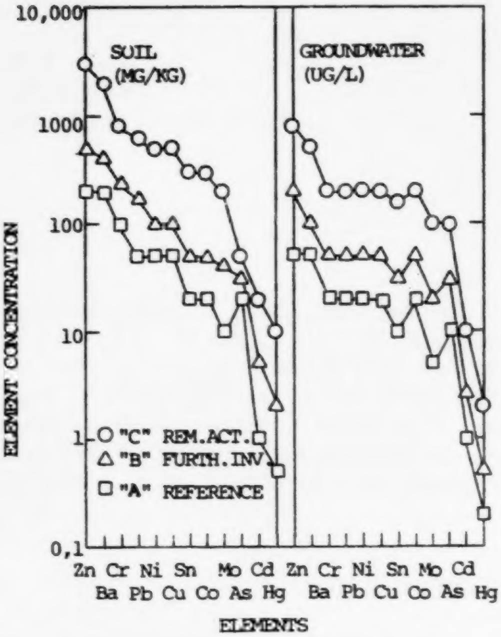


Figure 1. Indicative values for remedial action ("C"), further investigation ("B") and reference value ("A").

ESTABLISHMENT OF REFERENCE VALUES FOR A MULTIFUNCTIONAL SOIL

The reference values are based on an evaluation by the TCB of 118 soil samples collected from the top 10 cm in natural areas (Edelman, 1984) after removal of the mulch layer. On these areas no obvious harmfull effects resulting from the chemicals were observed and the soil was presumed to have retained its multifunctionality. A linear regression was established between the concentration of the element and clay content (percentage smaller than 2 micron meter and organic matter content as shown in Table 1. Some outliers were eliminated because of special circumstances (natural arsenic deposits, elevated copper and zinc at archeological sites, etc). The strongest correlations between the concentration of the element and the clay content were noted for Cr, Ni for all samples. The correlations for Cu, Zn, Pb and As improved considerably when only the "mineral samples" with an organic matter content below 250 g/kg were considered. The correlation between the organic matter content and the difference between concentration estimated from the clay content and the measured value (DE) was strongest for Cd, Zn and Pb. A comparison of the regression coefficient show that an increase in the organic matter content has a three times larger effect than an increase in clay content in predicting the increse in cadmium concentration (3.3:1). For Pb the ratio is 1.2:1 while for Zn and Hg it is 0.45:1 and 0.41:1, respectively. No relationship with organic matter content was found for As and Cu (although mineral samples had higher mean concentrations) and Ni and Cr (Figure 2.)

The background values from natural areas can be compared to data collected for uncontaminated pleistocure sands (Breeuwsma, 1986) and marine and river deposits (Salomons, 1983) as shown in Table 2. The values for the natural areas, extrapolated to zero clay content, (intercept value a) are generally higher than the pleistocene sands probably as a result of areal deposition. The regression coefficients with respect to clay content however, show a much closer agreement. The data also show the large difference between metal content in the mulch layer and the different horizons indicating the importance of specifying sampling depth.

The natural area data were used to establish an upper limit equal to two times the standard deviation in the relation between element concentration and clay content

TABLE 1. Relationship between element concentration and clay content or organic matter content for all samples, for "mineral" soil samples (H < 250 g/kg) and for "organic" soil samples (H) 250 g/kg).

element	samples	relation*	a	b	n	r	$s_{y.x}$
Cr	all	1	22,5	0,190	116	0,922	12,2
	mineral	1	21,2	0,205	89	0,917	12,5
	organic	2	--	--	--	--	--
Ni	all	1	0,707	0,0833	117	0,934	4,87
	mineral	1	-0,416	0,0911	89	0,954	4,04
	organic	2	--	--	--	--	--
Cu	all	1	3,55	0,0608	113	0,732	8,81
	mineral	1	1,41	0,0582	85	0,962	2,37
	organic	2	9,34	$0{,}27.10^{-3}$	30	0,004	14,9
Zn	all	1	27,9	0,236	93	0,771	31,0
	mineral	1	15,5	0,278	69	0,929	17,0
	organic	2	-39,4	0,125	26	0,608	40,3
Cd	all	1	0,333	$0{,}578 . 10^{-3}$	111	0,191	0,464
	mineral	2	0,157	$0{,}623 . 10^{-3}$	83	0,435	0,186
	organic	2	-0,197	$1{,}68 . 10^{-3}$	30	0,645	0,502
Hg	all	1	0,0676	$0{,}205 . 10^{-3}$	99	0,456	0,062
	mineral	1	0,0511	$0{,}181 . 10^{-3}$	79	0,503	0,045
	organic	2	0,0503	$0{,}079 . 10^{-3}$	22	0,269	0,069
Pb	all	1	27,0	0,0872	103	0,422	28,98
	mineral	1	15,8	0,0845	81	0,775	10,0
	organic	2	-3.8	0,095	24	0,609	30,4
As	all	1	4,25	0,0432	110	0,796	5,15
	mineral	1	3,03	0,0371	83	0,919	2,31
	organic	2	7,59	$0{,}33 . 10^{-3}$	29	0.012	0,83

*The linear regression is (1): E = a+bL, with E = element concentration (mg/kg), a = intercept, b = regression coefficient, L = clay or lutum content (g/kg) or (2): DE = difference between concentration estimated from clay content and measured concentration, a = intercept, b = regression coefficient, H = organic matter or humic content (g/kg). The number of observations (n), the correlation coefficient (r) and the residual standard deviation ($s_{x,y}$) are also shown.

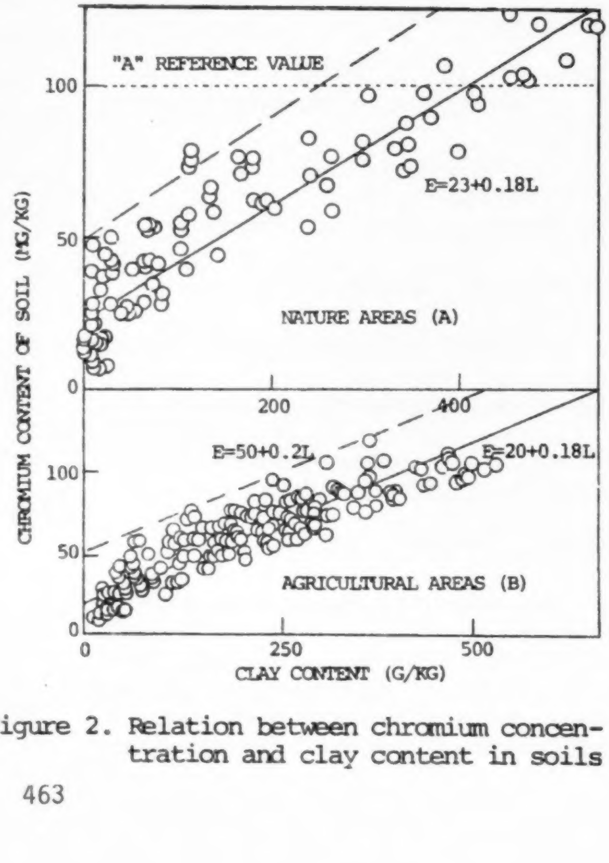


Figure 2. Relation between chromium concentration and clay content in soils

allowing an exceedance of 2.5%. These relations were compared with analysis results of 266-966 mineral soil samples (H below 250 g/kg) collected from the top 20 cm in agricultural soil (Van Driel and Smilde, 1982; Wiersma et al., 1985). The exceedance for Cr (Figure 2) and Ni was only 0% and 1%, respectively, (n=266), while for Cd it was 6% (n=965). For Pb, Zn and Hg it was 11%, 12%, and 13%, respectively. For As and Cu it was as much as 21% and 40%, respectively, reflecting use of copper containing chemical and fecal fertilizers and pesticides.

TABLE 2. Background Concentration's in Pleistocene Sands and Marine Deposits

Samples	Cr	Ni	Cu	Zn	Cd	Pb
			Content mg/kg			
Uncontaminated pleistocene sands (B_3, C, G horizon)	8,9	5,5	2,0	7,4	0,08	2,9
Natural Areas**	21,2	0,7	3,6	15,5	0,33	15,8
Marine deposits from Dollard estuary collected in 1922*	72	29	13	68	0,25	21
Marine deposits from Dollard endiked before 1880, collected from top 20 cm*	69	28	11	70	0,24	25
River deposits from Rhine polders endiked before 1780, collected from top 20 cm*	87	35	24	87	0,29	29
Concentration in different horizons in sandy soil:						
Ao: Mulch layer	13	8,5	27	122	1,3	161
A1: Humic top layer	13	2,2	3,2	14	0,31	23
B2: Precipitation layer	9,5	2,1	1,4	7,0	0,12	4,8
B3: Identical	9,0	3,1	1,4	7,0	0,08	2,7
C: Original material	8,8	4,2	1,8	7,1	0,07	3,1
			Regression Coefficient b with respect to clay			
Marine deposits	1,189	0,071	0,033	0,182	$0.51.10^{-3}$	0,054
River deposits	0,234	0,089	0,066	0,239	$0,63.10^{-3}$	0,078
Natural areas**	0,205	0,091	0,058	0,278	$0,62.10^{-3}$	0,085

* The values for marine and river deposits are standardized for a fine fraction (smaller than 16 um) of 50%.

**See Table 1 calculated from intercept.

ESTABLISHMENT OF REGULATORY SOIL LIMITS

In order to establish regulatory limits suitable for practical use simplification of the different relations in Table 1 is necessary. It is desirable to formulate one relationship that can be used for all elements. The general relationship is: a simplification of the different relations in Table 1 is necessary. It is desirable to formulate one relationship that can be used for all elements. The general relationship is:

$G_{ij} = a_i + b_i \cdot L_j + c_i \cdot H_j$ (1)
G_{ij} = concentration of elements in soil j. (mg/kg)
a_i, b_i, c_i = contents of element i
L_j = percentage clay in soil j.
H_j = percentage organic matter in soil j.

This can be simplified to:
$G_{ij} = C_{oi} (a + bL_j + c H_j)$ (2)
C_o: = reference value of element for standard soil
a,b,c = constants similar for all elements

The equation proposed by VROM (1986) selected the constants as follows:

$G_{ij} = C_{oi} (0.5 L_j + 1.5 H_j)$ (3)

The value of the organic matter in (3) is weighted 3 times more than the clay content. From Table 1 it can be seen that this only is the case for Cd and that for other elements the organic matter influence is much lower. A disadvantage of (3) is that it underestimates the metal content in sandy soil with a low clay content (resulting in high exceedance of the regulatory limit) and overestimates the value in organic soils (resulting in a filling up of the norm.)

The TCB therefore proposed as an improved equation:

$G_{ij} = C_{oi} (10 + 0.5 L_j + 0.25 H_j)$ (4)

In this equation the organic matter contributes only half as much as the clay content to the estimated element concentration, while the intercept constant a results in values closer to the analytical results in sandy soil. The reference values for "standard" soil (H:10%; L:25%) are given in Figure 3. The G_{ij} values for other soils are derived from the value of the standard soil by multiplying the reference value C_{oi} by $(0.5\ L_j + 1.5\ H_j)/27$ according to (3) and by $(10 + 0.5\ L_j + 0.25H)/25$ in (4). The results for sandy soil, clay soil and organic soil are shown in Figure 3. The agreement between measured value and predicted value using (4) is quite good and is therefore suitable for regulating purposes in evaluating contaminated soils and directing cleanup operations.

ESTABLISHMENT OF REGULATORY GROUNDWATER LIMITS

Regulatory limits or reference values that are not to be exceeded were also proposed for groundwater. The values were based on the analytical results of the country wide shallow groundwater monitoring network (Van Duyvenbooden et al., 1984) and on theoretical equilibrium calculations (VanHeck and Wassenberg, 1984) as shown in Table 3. The largest overestimation was noted for Hg. The observed values were also compared with the average rainfall concentrations (using both dry and wet deposition data) and infiltration concentrations using a three fold concentration increase as a result of evapotranspiration (Rivm, 1984). The measured values are generally below the calculated infiltration concentrations indicating substantial adsorptive processes in the soil especially for Cu, Zn and Pb. For As the reverse was observed, likely resulting from As upwelling from deeper marine deposits. The proposed VROM and TCB regulatory limits allow for a 5-10% exceedance. As soluble concentrations vary greatly because of variations in pH, ORP, and complexities, a differentiation according to clay content and organic matter was not feasible.

EFFECT -BASED REFERENCE VALUES

The above proposed approach to establish reference values for a multifunctional soil uses the upper limit of the currently observed ranges in relation to specific soil parameters in soils that are not polluted ("preserving current quality"). An

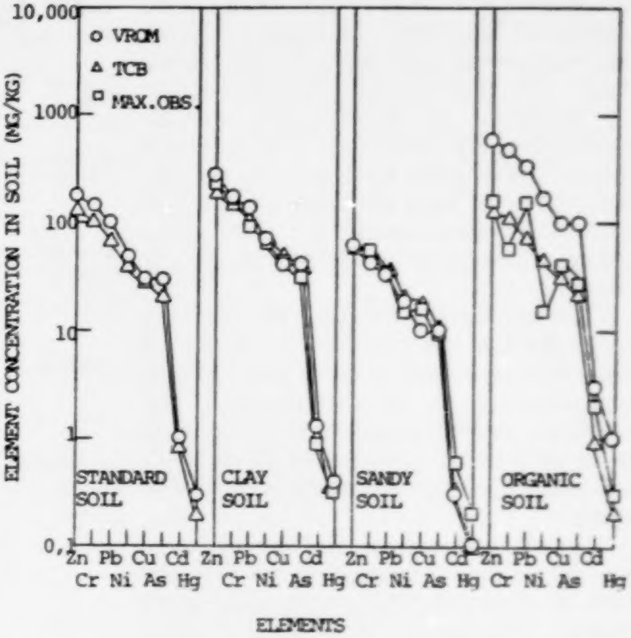


Figure 3. Element concentrations predicted by the VROM and TCB model and maximum observed concentrations for different soils.

TABLE 3. Concentration in groundwater and proposed reference values (ug/l).

Element	Mean Concen. of Groundwater Monitoring Network	Concen Exceeded by 10% of Samples	Theoretical Equilibrium Concen.	Mean Concen. in Rainwater	Mean Concen. of infiltration water after Evapotranspiration	Proposed Refer. Values by VROM	Proposed Refer. Values by TCB
Cr	0,7	1,0	4	0,5	1,5	5	1
Ni	3,2	16	3	1,5	4,5	10	15
Cu	5	14	4	7,5	22,5	10	15
Zn	30	150	26	53	160	70	150
Cd	0,4	2,4	0,7	0,4	1,2	1	2
Hg	0,02	0,03	0,3	0,02	0,06	0,2	0,05
Pb	4,8	7	25	13	39	15	15
As	3,0	5,4	7	0,8	24	10	10

alternative approach evaluates each of the multiple soil functions with respect to dose-effect relationship and level of irreversible damage. The most sensitive function is then used as limit to protect the overall multifunctionality of the soil. This approach was not chosen at this time, but may be used when sufficient data for each of the soil functions become available. For some elements, however, this approach can already be taken.

The ecological function was defined through the functioning of the detrital food chain, often representing more than 90% of the production in an ecosystem. The saprophage invertebrates were evaluated with respect to nutrient cycles and food chain accumulation of the biologically available portion.

No effect levels for Cu were observed below 60 mg/kg for *Lumbricis rubellus* and below 30 mg/kg for *Allolobophora longa* whereby coconproduction was a more sensitive indicator than mulch decomposition. A pH increase greatly increased no-effect levels. The no-effect-level for Cd was 20 mg/kg for *L. rubullus*. The isopod *Percellio scaber* showed no effect levels for juvenile production at 2000 mg/kg Zn and 10 mg/kg Cd, and for mulch consumption at 1500 mg/kg Zn and 2 mg/kg Cd. The collembol *Orchesella cincta* showed no effect levels of 64 mg/kg for Cd. All of the above concentrations reflect values in the upper mulch layer which are higher than the average concentrations in the top 10 cm of the profile (Table 2).

All investigated oligochaets, isopods and collembols accumulated several metals especially Cd and to a lesser extent Zn possibly leading to further food chain accumulation.

The public health effects of contaminated soil were considered through summation of six exposure routes through which the soil contaminants could reach humans. The approach followed that used by Van Wynens (1982) and Verwy and Luiten (1984). The multimedia model assumes a proportionality between mass flux (human intake) and soil concentration as shown in Table 4. It was also assumed that the total intake originating from contaminated soil corresponded to 50% of the ADI with the remaining 50% allocated to other intakes such as smoking and industrial exposures. For Cd the corresponding soil concentration was calculated to be 0,36 mg/kg which value is slightly below maximum observed reference soil concentrations.

TABLE 4. Calculation of Cd Soil Concentration Limit Corresponding with Cd Intake of 50% of ADI through Six Exposure Routes

Exposure Route	Relation	Paramaters	Selected Values
Soil/Dust Ingestion	$x_1=a_1.f_1.y$	x_1=rate through soil ingestion (mg/person.day)	
		f_1=uptake + correction child/adult (kg/person.day)	5 x 0,2
		a_1=transfer coefficient (-)	0,0002
		y=soil concentration (mg/kg)	
Drinking Water	$x_2=a_2.f_2.y$	x_2=rate through drinkng water ingestion (mg/ person.day.	
		a_2=soil desorption coefficient (-)	0,002
		f_2=drinking water factor (kg/person.day)	2
		y=soil concentration(mg/kg)	
Vegetable	$x_3=a_3.f_3.y$	x_3=rate through vegetable ingestion (mg/person. day)	
		a_3=transfer coefficient soil/crop (-)	0,02-0,1
		f_3=vegetable consumption (kg/person.day)	
Meat/Milk/ Eggs	$x_4=a_4.f_4.y$	x_4=rate through meat ingestion (mg/person.day)	
		a_4=transfer coefficient soil/crop/animal (-)	0,147
		f_4=consumption (kg/person.day)	0,279
Fish	$x_5=a_5.f_5.y$	x_5=rate through fish ingestion (mg/person.day)	0,012
		a_5=transfer coefficient soil/water/fish (-)	
		f_5=fish consumption (kg/person.day)	0,014
Breathing	$x_6=a_6.f_6.y$	x_6=rate through inhalatin (mg/person.day)	< 10-7
		a_6=transfer coefficient soil/air and dilution (kg/m^3)	
		f_6=inhalation volume (m^3/person.day)	12
Total	$x_t=c_t y$	x_t=50% of ADI for soil routes (mg/person.day)	0,064
		c_t=overall coefficient (kg/person.day)	0.09
		y=soil concentration limit (mg/kg)	0,36

The effects of soil contamination on the crop growing function of the soil was extensively evaluated (LAC, 1985) and signal values or criteria were developed above which a crop yield reduction could take place or whereby the human health through crop consumption could be harmed. The values for the different elements are Cd: 0,5-1,0 mg/kg (human consumptive), Cu: 30 mg/kg (yield reduction), Pb: 100-150 mg/kg (human consumption/yield reduction), Hg:2 mg/kg (human consumption); Zn:100-350 mg/kg (yield reduction), in which the lowest value in the range applies to sandy soil and the highest value for clay and organic soils. These values are in agreement with the reference values developed earlier.

SOIL QUALITY DETERIORATION AND REMEDIATION

The proposed reference values representing the upper limits of the currently uncontaminated soils (with 2.5% excellance) are expected to be exceeded in the future if input through sludge and compost application and fecal fertilizers is not greatly restricted (Table 5.) Steps to restrict these diffuse inputs are currently being taken.

The number of soils classified as contaminated by hazardous waste and point sources will increase because the reference values are lower than the earlier established "A" values used to designate the sites. Most remedial technologies developed in the Netherlands that use separation, washing and leaching techniques have generally been able to reduce the inorganic elements to the "B" values shown in Figure 1. However the "A" value or the above discussed reference values have generally not been met, indicating that the use of the cleaned-up soil is not unrestricted and is still subject to ICM criteria.

CONCLUSION

The present study established reference values for uncontaminated soils in relation to its clay and organic matter content. These reference values are to be used to designate soils that are contaminated by hazardous waste and releases from point sources. In addition, they will be considered as cleanup goals (but not as legal standards) to be reached by soil remediation techniques. The limited dose-effect relationships for the different soil functions indicate levels comparable to the reference values. Reference values for organic substances (27 chlorinated hydrocarbons, 13 polycydic aromatics and total alkanes) were also developed in relation to the organic matter content of the soil. Because of the limited data and numerous assumptions, the results are presented elsewhere (TCB, 1986).

TABLE 5. Input and Output of elements on agricultural soil

	input (g/ha/yr)			output (g/ha/yr)		
Element	Deposition	Sludge & Compost	Fecal Fertilizer	Leaching	Plant Uptake	Period in which Concentration doubles (years)*
Zn	400	4000	1080	300-500	100-500	50-60
Cu	60	1200	625	20-70	30-1650	25-30
Pb	100	1000	20	30-60	1-80	120-160
Cr	4	1000	--	10-15	1-10	190
Ni	10	200	35	45-70	10-30	500-700
Cd	3	10	2	2	0.3 - 8	120-300
Hg	0.2	10	0.12	0.2	0.2 - 1.5	45-50

*Period in which concentration in top 20 cm doubles from half of reference value to full reference value for standard soil.

REFERENCES

Biemond, C "The use of the soil," in "Handbook for Environmental Mangement" Edit." VandenBerg C. et al., Vermande Zonen/Samson Publ. Alphen aan de Ryn(1978).

Breeuwsma A "Background values for metals in pleistocene sandy soils; contribution to TCB task force" Institute for Soil Cartography, Wageningen (1986).

EC: European Community "Water quality standards for drinking water, EC directive" EC Publications Journal, L229-11(1980).

Edelman T "Background concentrations of a number of inorganic and organic substances in dutch soil," Ministry of Housing, Physical Planning and Environment, Soil Protection Series 34, Governmental Printing Office, The Hague (1984).

LAC, Agricultural Advisory Committee on Environmentally Critical Substances "Signal values for concentration of environmentally critical substances in the soil with respect to agricultural use of polluted soil, Minsterty of Agriculture The Hague (1985).

Moen JET, Cornet JP, Evers, CWA "Soil protection and remedial actions: criteria for decision making and standarization of requirements" in "Contaminated Soil" Ed. Assihk JW and VandenBrink WJ, Martinus Nyhoff Publ. Dordrecht (1986)

Nypels ETHM "Opening Speech Soil Quality Symposium," Minister of Housing, Physical Planning and Environment, The Hague (1986).

Rivm, State Insitute for Public Health and Environmental Hygiene "Monitoring network for rain water, summary and statistical evaluation of the analytical results" Bilthoven/Leidschendam (1984).

Salomons W "Preliminary baseline values for Cd, Zn, Ni, Pb, Cu, and Cr in Dutch sediments" Report R1703, Hydraulics Laboratory, Delft (1983).

TCB: Technical Commission on Soil Protection "Recommendation for Soil Quality" Ministry of Housing, Physical Planning and Environment, The Hague (1986).

VanDuyvenbooden W, Gast LFL, Taat T "Country wide groundwater monitoring network, final report of the settup phase" Ministry of Housing, Physical Planning and Environment, Soil Protection Series 46A, The Hague, Governmental Printing Office (1984).

VROM: Ministry of Housing, Physical Planning and Environment" Is our soil the forgotten son," The Hague, (1986).

Van Driel W. and Smile K. W. "Heavy metal contents of dutch arable soils" Landwirtsch. Forsch. Sonderh. 38, 305 - 313 (1982)

Van Heck B and Wassenberg W "Groundwater contamination from industrial activity" M. Sc thesis, University of Utrecht (1984).

Van Wynen JH "Evaluation of the health risk in a case of soil pollution (Volgermeer)" Tydschr. Soc. Geneesk. 60 (1982).

Verwey GCG and Luiten JA "Significance and use of reference framework, concentration measurements and characteristics of substances in the evaluation of soil contamination" RIVM, Report 840224002, Leidschendam/Bilthoven (1984)

Wiersma D, Van Goor BJ, VanderVeen NG "Inventory of cadmium, lead, mercury and arsenic in Dutch crops and related soils" Institute for Soil Fertility, Report 8-85, Haren (1985).

Land Treatment of an Oily Waste -- Degradation, Immobilization and Bioaccumulation

Raymond C. Loehr
Civil Engineering Department
The University of Texas
Austin, TX 78712

John H. Martin, Jr.
Agricultural Engineering Department
Cornell University
Ithaca, New York 14853

Edward F. Neuhauser
Niagara Mohawk Power Corporation
Syracuse, NY 13202

ABSTRACT

Land treatment of an industrial oily waste was investigated to determine the loss and immobilization of waste constituents and the impact of the waste and the application process on soil biota. The waste was applied to field plots of a moderately permeable silt loam in New York. The plots consisted of four replicates of natural controls, rototilled controls, and each application rate. Wastes were applied in 06/82, 10/82, and 06/83 and at seven waste application rates that ranged from 0.09% to 5.25% oil and grease in the zone of incorporation.

The applied wastes increased the pH and volatile matter of the soils. The half-life of the total oil and grease ranged from about 260 to about 400 days. Not all of the applied oil was lost. The refractory fraction did not appear to adversely affect the soil biota. Napthalenes, alkanes and specific aromatics were rapidly lost from the soil. The half-life of these compounds generally was less than 30 days.

The waste applications increased the metal concentration in the upper 15 cm of the soil. Except for sodium, all of the metals were immobilized. These wastes did not cause any unexpected bioaccumulation of metals in the earthworms. The earthworms did not accumulate napthalenes, alkanes, or specific aromatics that were in the applied waste. Rototilling and waste application initially reduced the numbers and biomass of earthworms in the field plots. The soil biota were able to recover from these perturbations.

INTRODUCTION

Land treatment is a managed waste treatment and ultimate disposal process that involves the controlled application of a waste to a soil. The wastes are applied to the surface or mixed with the upper zone (0-1 ft. (0-0.3 m)) of soil. Land treatment: (a) results in the biological degradation of organics and the immobilization of inorganic waste constituents, and (b) utilizes the assimilative capacity of the soil.

Land treatment has been used as a waste management technology by petroleum refineries in the United States for more than 25 years, as well as by other industries. The major concerns when land treatment is used for industrial wastes are the transformations, transport and fate of potentially toxic metals and organics that may be in the wastes.

As identified in the Resource Conservation and Recovery Act (RCRA), land disposal methods are to be protective of human health and the environment. The factors to be taken into account in assessing such protection are the persistence, toxicity, mobility and propensity to bioaccumulate hazardous wastes and their constituents.

Except as part of organic degradation, the soil biota rarely have been included in any land treatment system evaluations. However, the top layer of soil contains myriad microbes and invertebrates that degrade and transform the applied organics. In the terrestrial food chain, earthworms represent one of the first levels of bioaccumulation that can occur when wastes are applied to the land. Therefore, in this study earthworms were used as a test organism for determining the impact of industrial waste on soil biota when land treatment is used for such wastes.

PURPOSE

The purpose of this project was to determine: (a) the loss and immobilization of constituents of an oily waste when the waste was applied to the soil at different application rates, (b) the impact of the waste and the application process on earthworms, and (c) the general assimilative capacity of a soil when industrial wastes are land applied.

APPROACH

Cooperation -- This project was a cooperative agreement between Cornell University and the Robert S. Kerr Environmental Research Laboratory (RSKERL) of the Environmental Protection Agency (EPA). The research was conducted in laboratories of the Department of Agricultural Engineering, Cornell University, and on land adjacent to the Cornell campus.

Wastes -- The wastes were obtained from a site in Oklahoma with the help of RSKERL personnel. The wastes were black, viscous, and collected from the bottom of a lagoon used to store wastes from oil refineries. The wastes were applied to the field plots at different application rates. Samples of the wastes were analyzed before each application date, and the oil data used to determine the volumes of waste to be added to achieve the desired loading rates.

These oily wastes had been contained in the lagoon for several years before the required quantities were removed and transported to the field site for application. Many volatile compounds may have been lost while the wastes were in the lagoon.

Field Site -- The site used for application of the waste was an old field in Tompkins County, New York. It had not been used for agricultural purposes and had not received lime, fertilizer, pesticides or herbicides for over 10 years before its use in this project. The soil at the site was a Rhinebeck silt loam. The soil was moderately permeable, had a cation exchange capacity of 24.8, and exists on nearly level to moderate slopes in glacial lake areas.

The field site consisted of 20 plots, 4 meters by 4 meters, with 4 meters of border area surrounding each plot. Natural and rototilled controls were used at the site. Four replications were made for each waste application rate and type of control. All plots were mowed before each waste application. All plots, except the natural controls, were rototilled after each application of the waste. The four rototilled control plots had no waste applied but were rototilled. The four natural control plots had no rototilling or waste applied and were used to separate the effect of the rototilling and the waste applications. The applied wastes were distributed over the plot surface as uniformly as possible and were rototilled into the soil such that the zone of incorporation (ZOI) was the top six inches (15 cm).

Each test plot (16 m^2) was marked with corner stakes to permit placement of a grid to define 400, 20 cm by 20 cm sampling subplots. Three different subplots were sampled on each sampling date to determine changes in ZOI characteristics and in earthworm populations. To eliminate edge effects, no edge subplots were sampled. The subplots that were sampled were determined using a random number table. Thus, different sampling locations were used at each plot each time samples were taken. No subplot was sampled twice during the study. An elevated plank platform was used for sampling so that the plots were not disturbed or contaminated while the samples were taken.

Natural vegetation such as grass was allowed to grow on the plots after the waste applications. Native grasses did re-establish themselves on all of the plots in the months after the wastes were applied.

Soil cores were taken from each plot at approximately monthly intervals except during the winter. Hand sorting was used to determine earthworm numbers and biomass from each core. Before the characteristics of the ZOI were measured, the cores from each plot were composited. Residual soil was returned to the plots and used to fill in the core holes.

Analytical Procedures -- Metals and certain organics in the waste, soil and earthworm samples were analyzed by personnel at RSKERL, using ICAP, GC and GC/MS procedures as appropriate. Cornell personnel analyzed the waste and soil samples for more routine parameters using *Standard Methods* or comparable procedures.

Special Studies -- Two special studies were conducted to determine the variability in the characteristics of the ZOI and the precision and accuracy of the analytical method used for oil and grease when used with soil samples. The spatial variability study identified the extent to which the variability of the data was due to the non-homogeneity of waste application and rototilling. The results of these studies have been published (1,2).

Waste Application -- Table 1 identifies the application rates, dates of application and the plots that received the wastes. One set of plots received wastes three times at progressively larger rates. Another set received wastes twice. The effect of seven application rates, covering those likely to be used under actual field conditions, was evaluated.

Only the indigenous nutrients and trace elements in the soil and the waste were available to the micro- and macoorganisms as the wastes were degraded. No fertilizers or other amendments were added to the plots. The plots were only cultivated (rototilled) immediately before and after the wastes were applied. No subsequent cultivation occurred to aerate the ZOI. This approach was taken in order to approximate the changes that would occur under conservative and nonoptimum conditions such as when single or highly intermittent waste applications are administered or when a spill occurs. The approach also caused one less variable, the frequency and type of aeration (tilling) to be included in the study.

TABLE 1 -- FIELD PLOT APPLICATION RATES

Date of Waste Application	Average Oil Application Rate (kg oil/m^2)	Field Plot Number+
June 1982	0.17	5, 6, 12, 18
	0.34	4, 10, 11, 17
	0.68	2, 8, 14, 20
October 1982	1.46	5, 6, 12, 18
	2.74	4, 10, 11, 17
	4.55	2, 8, 14, 20
June 1983	9.5	5, 6, 12, 18

+ Plots 1, 7, 13 and 19 were natural controls and plots 3, 9, 15 and 16 were rototilled controls.

RESULTS

The pH of the plots that received the high applications of the oil waste increased. The increase was pronounced for the plots that received the very high applications in 06/83 (Figure 1). In these plots, the soil pH increased by more than one unit from below 6.0 to about 7.0 After the waste applications, the pH stayed at above background levels for the remainder of the study. An evaluation in April, 1986, almost three years after the last application, indicated the pH in the very high application rate plots continued to remain higher than the controls and had a value of 6.7.

The volatile matter in the soil was increased by applying waste. Until the larger waste applications in 10/82, the volatile matter in all the plots was about 9% of the soil on a moisture free basis. After the 10/82 application, the volatile matter in the plots increased to 10 to 11%. After the application in 06/83, the volatile matter in the very high application plots was 14 to 15%. In April, 1986, volatile matter in the very high plots was 12.8%, indicating that there had been little loss of the residual organic matter in three years. The loss that did occur represents natural degradation processes.

With time, the concentration of oil and grease in the soil decreased. The pattern of loss is illustrated in Figure 2 for the oil and grease in the high application plots. However, the applied oil and grease was not lost completely. After each waste application, a new apparent background concentration in the respective plots resulted.

It was impossible to correlate statistically the oil and grease losses to the field plot soil temperatures. Any effect due to temperature was masked by factors such as the variability in the oil and grease data, differences in soil moisture as the soil temperature changed, and differing oil and grease compounds in the soil during the study.

The immobilization of metals in the soil was analyzed by comparing the metal concentrations of subsoil samples from the 15 to 30 cm depth taken in 10/83. The concentrations of Al, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, Va and Zn were analyzed statistically to determine if the deeper soils of the controls and the waste application plots had differing metal concentrations. The analysis indicated that sodium was the only metal with a significantly different concentration in the 15 to 30 cm depth between the control plots and any waste application plot. That difference only occurred for sodium in the soil of the very high plots.

Soil samples from the plots were taken at intervals of one month or more to determine the loss patterns of specific organics. The samples were extracted with methylene chloride and the extracts analyzed for C_8 to C_{26} alkanes, napthalenes, and aromatics such as fluorene, anthracene, phenanthrene and pyrene.

The half-life of organics applied to the soil varied. The loss of specific organics (napthalenes, alkanes, and certain aromatics) was rapid, especially in the warmer months (Table 2). The half-life of these compounds was generally less than 30 days. In comparison, the half-life of the total oil and grease in the field plots ranged from about 260 to about 400 days.

All of the applied organics were not lost from the soil during the study. The separation and identification procedures used were not able to identify the type or structure of the residual organics that remained in the soil at the end of the study. However, based on laboratory studies using soil from the field plots and the fact that earthworms could repopulate the soil of the plots receiving the wastes, the organics remaining in the soil did not appear to result in a permanent adverse impact to the soil biota.

The application of the wastes had definite effects on the earthworm numbers and biomass in the field plots, due to both the rototilling and the immediate impact of the waste. The earthworms were decreased by the rototilling and even more so

TABLE 2 -- LOSS OF ORGANIC COMPOUNDS FROM FIELD PLOTS

Compound	Average Half-Life (Days)	Compound	Average Half-Life (Days)
Napthalene	R*	C_{13} alkane	10
2-methyl napthalene	18	C_{14} alkane	13
1-methyl napthalene	12	Fluorene	12
1,3-dimethyl napthalene	8	Anthracene	R
2,3-dimethyl napthalene	10	1-methyl-phenanthrene	77
C_{12} Alkane	13	Pyrene	10

*rapid, loss to below detectable limits occurred in less than one month after application

by the wastes. However, with time, earthworms did repopulate the field plots (Figure 3). Evaluation in April 1986 showed a dramatic increase in earthworm numbers and biomass in all the plots, and especially in the very high application rate plots. The project results indicate that these soil biota can recover from the addition of oily wastes.

The earthworms in the plots accumulated cadmium, potassium, sodium and zinc. Potassium and sodium are of physiological but not environmental importance in terms of bioaccumulation. The cadmium that accumulated in the earthworm tissue came more from the background cadmium in the soil than from the cadmium in the applied waste, since the cadmium bioaccumulated at comparably high levels in the worms from the control plots. A comparison of the data from the peer-reviewed literature indicated that the land application of these oily wastes did not cause any abnormal or unexpected bioaccumulation of metals in earthworms.

Earthworm samples were analyzed for the same organic compounds that were determined for the soil extracts (alkanes and certain aromatics). None of these compounds were found in the earthworm methylene chloride extracts at concentrations greater than the detection limits.

CONCLUSIONS

The results indicated that the soil has the capacity to treat wastes such as those used in this study. Many of the organics in the applied waste were removed (lost) and the metals were immobilized when the wastes were applied to the soil intermittently and at varied rates. The soil cultivation method (rototilling) and the applied waste had an immediate adverse impact on the earthworms, but they recovered with time. A fraction of the applied oil and grease was not removed during the study. The remaining organics and the metals did not appear to have any permanent adverse effect on the soil biota.

The study indicated that soil biota can recover from intermittent applications of an oily waste. With time, the numbers and mass of earthworms in the plots to which the wastes were applied can become similar to those in the control plots. The land application of these wastes did not have an irreversible, adverse impact on the earthworms.

ACKNOWLEDGEMENTS

The assistance of staff and students at Cornell University, of the EPA Project Officer, Mr. John E. Matthews, and of the personnel at

RSKERL who analyzed the samples for metals and organics is gratefully appreciated.

The complete project report is available and can be obtained from the National Technical Information Service, Springfield, VA, 22161 (Order No. PB-166353/AS).

REFERENCES

1. Martin, J.H., Jr., and R.C. Loehr, "Determination of the Oil Content of Soils," *Hazardous and Industrial Solid Waste Testing: Fourth Symposium, ASTM STP 886*, J.K. Petros, Jr., W.J. Lacy and R.A. Conway, Editors, American Society for Testing and Materials, Philadelphia, 1986, pp. 7-14.

2. Loehr, R.C., Martin, J.H., Jr., and E.F. Neuhauser, "Spatial Variations of Characteristics in the Zone of Incorporation at an Industrial Solid Waste Land Treatment Site," *Hazardous and Industrial Solid Waste Testing: Fourth Symposium, ASTM STP 886*, J.K. Petros, Jr., W.J. Lacy and R.A. Conway, Editors, American Society for Testing and Materials, Philadelphia, 1986, pp. 285-297.

DISCLAIMER

Although the research described in this article has been funded wholly or in part by USEPA, the article has not been subject to Agency review and therefore does not necessarily reflect views of the Agency and no endorsement should be inferred.

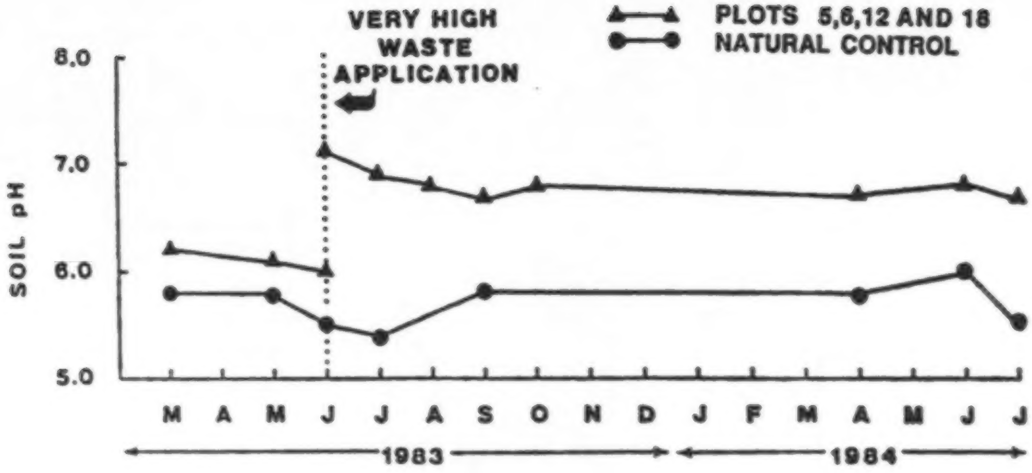


FIGURE 1

pH of the Soil in Several of the Field Plots

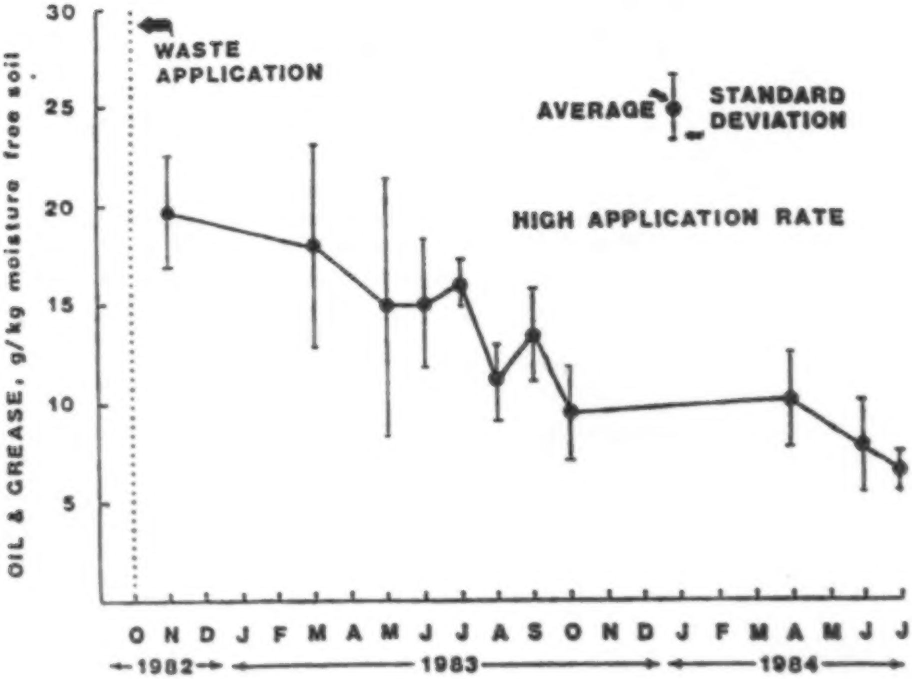


FIGURE 2

Oil and Grease Concentrations in the Soil of Field Plots 2, 8, 14 and 20

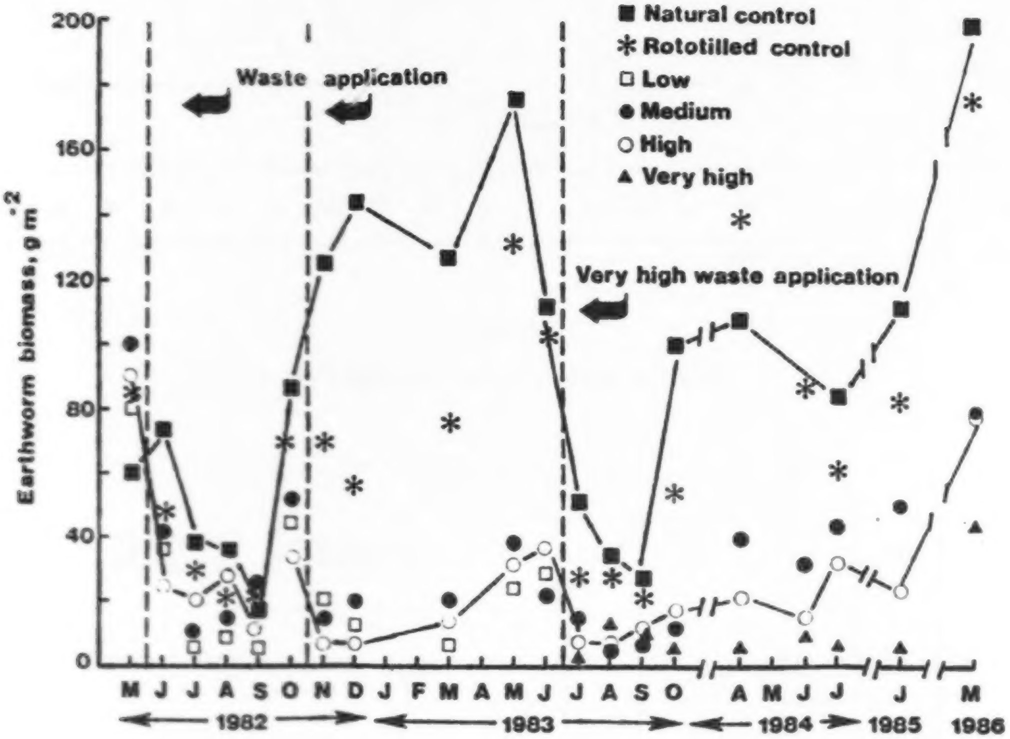


FIGURE 3

Earthworm Biomass in the ZOI of the Field Plots

THE USE OF CONTAMINATED MATERIAL FOR THE CREATION OF NEW HOUSING LAND AT THAMESMEAD, LONDON.

George W. Lowe
London Scientific Services
The County Hall
London SE1 7PB.

ABSTRACT

Re-development of the Royal Arsenal in Woolwich, London, to form the new town of Thamesmead has required the reclamation of 1000 acres of derelict industrial land lying at a considerable distance from disposal facilities able to receive contaminated material of the quantity arising from the development. This could have caused serious financial and logistical problems if advantage had not been taken of new river wall construction associated with the Thames Barrier and the London Flood prevention scheme. The river wall was constructed in the bed of the River Thames enclosing a large area of silt normally exposed at low tide.

Space formed between the new river wall and the old river embankment provided an opportunity to create new land using excavated material from construction sites known to be polluted by industrial waste from the Arsenal. Licences were granted for two disposal facilities to receive a total of 800,000 cubic metres of contaminated soil.

The first facility containing 350,000 m^3 is now ready for new housing development. On completion of filling and prior to final consolidation by surcharging, the land was investigated as if it were an existing contaminated site. The data obtained demonstrated a remarkable amelioration of the contamination due to mixing and consolidation techniques adopted during deposition and the result is new housing land requring little remediation to make it safe. The savings made in disposal costs are impossible to calculate at the present time but they are of the order of 5 million pounds stirling.

INTRODUCTION

Background - Development of Contaminated Land.

The decision to make use of contaminated material to create new housing land at Thamesmead did not form part of the original thinking when development of the new town was envisaged. At that time, there was little to suggest that new building would be seriously effected by ground conditions arising from industrial contamination, although there was some concern about mislaid explosives and unexploded bombs remaining in the ground from wartime air attacks.

Ground pollution problems began to manifest themselves in 1975 when advance civil engineering work started at the western extremity of the development where major armaments manufacturing and testing facilities had been concentrated. At the same time, problems associated with re-development of contaminated land began to achieve a prominence in London on a scale not previously experienced. This was mainly due to increasing demand for new development land at a time of serious land shortage in the inner city areas. This in turn led to the re-use of derelict land remaining from the decline of traditional and often noxious industries, rationalisation of transportation systems and changing patterns of energy demand and provision. Sites such as these had never been much in demand for re-development except in locations where site values were so high as to overide the financial significance of reclamation.

In common with the controlling public authority for Thamesmead, the developers of contaminated land in London were confronted with the need to arrange safe disposal of surplus excavated material arising from civil engineering and general construction work. The Control of Pollution Act 1974 was only just beginning to have an effect, licencing procedures for disposal sites were in their early stages and not fully understood, and the construction industry had yet to fully grasp the significance of emerging regulations. Most importantly, it soon began to emerge that regardless of transportation costs, available disposal options were likely to be severely restricted due to lack of capacity. (1)

These problems compelled developers and contractors to address their attention to the disposal of excavated waste from their sites as a fundamental part of their operations, rather than dealing with it as a consequence of construction to be relegated to sub- contractors with the lowest possible transportation rates, dubious disposal arrangements and a commensurate disregard for the environment.

The scale of the operation at Thamesmead demanded an approach to disposal of contaminated material which would take into account ever increasing costs of transportation to limited disposal facilities, risks to the environment generally and the inconvenience to newly occupied households. Additionally, the perceived social impact of long term, large scale development likely to be felt in the surrounding areas prompted Local Authorities to place restriction on the routes and movement of heavy vehicles carrying materials to and from the site.

Fortunately, the Planning and Design teams for Thamesmead were able to take advantage of comprehensive project management with a direct line to policy making committees of the Greater London Council under whose auspices the development of the town was taking place. Opportunities thus arose to profit from circumstances both external and apparently unrelated to Thamesmead and find a very successful solution in financial and environmental terms to a seemingly intractable problem. A more positive response to re-cycling proposals was also beginning to emerge which was also very useful.

The London Flood Prevention Scheme.

Thamesmead has a frontage onto the River Thames of approximately 3½ miles (5.6 KM) and in consequence has been significantly influenced in its plan form by major civil engineering works associated with the London flood prevention scheme. The principle component of the scheme is the Thames Barrier which was completed in 1985 and was at that time, the world's largest movable flood barrier. Downstream, the embankments of the river have been raised to accommodate tidal surges originating in the North Sea. Where appropriate, new stretches of river wall have been constructed entirely, and there is a section of this at Thamesmead approximately 1 mile (1.6KM) in length.

Studies of the flow characteristics of the Thames indicated that the ideal location for this section of the river wall was in the bed of the river itself, sited to enclose a section of foreshore composed of deep, hazardous silt which became exposed at low tide. The maximum distance of the new wall from the original embankment is approximately 150 metres and although this reduces to zero at its conjunctions with the bank at each end, the crescent shaped area of re-claimed river bed thus formed is approximately 40 acres in extent. This presented an opportunity for the provision of major facilities at Thamesmead to serve the internal flood control system of the town itself and provide two disposal sites for contaminated material arising from construction works.

PURPOSE

On discovery of ground pollution at Thamesmead and knowing the difficulties encountered with re-development of contaminated sites elsewhere, the Planning and Design Teams were instructed by the Council to undertake initial studies to determine the geographical extent of the problem, the implications it would have on development, and in the longer term to undertake site by site investigations leading to remedial action. (2). A specialist team was established composed primarily of medical, scientific and technical officers who were soon to encounter the difficulty of making an overall assessment of ground pollution when the previous land use was almost totally classified (no information!).

APPROACH

An essential requirement of the team was to make an assessment of the overall, physical influence of ground contamination on the development form and programme with particular emphasis on costs arising from increased muck shifting and disposal. Following extensive calculations based on a number of area planning scenarios it became very clear that the cost and the impact on the environment of exporting possibly 1½ million cubic metres of contaminated material to out-county disposal facilities was totally unacceptable. Other enquiries had also established that even if the environmental impact question was set aside, the capacity of exisiting disposal sites was too uncertain to guarantee their availability in the long term.

Under the circumstances, disposal within the confines of Thamesmead became the only viable alternative, and it was fortunate for the development as a whole that the opportunity to use the spaces being created by the construction of the new river wall would be turned to positive advantage.

Procedures

Before the disposal facilities could be established, a number of difficulties had to be overcome both in practical and managerial terms. Not least of these was the provision of sufficient data to obtain a licence under the recently promulgated-Control of Pollution Act before the full nature and extent of ground pollution had been established. Another was to lay down criteria for control and management of the disposal facilities so that on completion of filling and consolidation they would provide development land whose general environmental condition was no worse than that of contaminated sites elsewhere in Thamesmead prior to rehabilitation.

A period of approximately 15 months was seen to be available for extensive site investigation work before programmed development of contaminated land created the need for disposal of substantial quantities of excavated material. During this time, data from site investigation provided enough information for the site licencing authorities in the GLC to assess levels of those substances forming the greater part of the contamination at Thamesmead which could be included in the mass of disposal material.

The conditions of the disposal licence also demanded a form of management for the facilities which was not compatible with normal construction contract procedures, but was achieved by placing site supervision, administrative control and the programming of filling in the hands of the Thamesmead management teams.

Controls

Probably, the most significant factor in the operational control of the disposal facilities was the ruling that no material would be accepted unless removed from sites which had been subject to full investigation. All investigation data was subject to scrutiny by a multi-disciplinery panel of specialists including those concerned with assessement of hazardous waste and site licencing procedures. By these means, the disposal facilities only received material from sites whose general level of contaminaton was acceptable under the terms of the licence. This to some extent was to influence development form.

Physical Influences

The major physical influence on the eventual condition of the facility was the condition introduced into the licence for ground consolidation purposes which demanded that material was spread, levelled and compacted in layers of 9 to 12 inches (225- 300mm) deep. In practice, this meant that one vehicle load of say 20 cubic metres would be spread over an area not less than 80 square metres in area. The value of mixing and dilution of the material under these circumstances is clearly very great especially when it is realised from the examination of the available data that a significant proportion of excavated material from polluted sites may not be seriously contaminated.

PROBLEMS ENCOUNTERED.

The majority of the problems encountered arose from programme fluctuations when filling the first facility, (4J/4K). As this meant that no material would be received for disposal for several weeks on end, the work force and heavy plant were deployed elsewhere. By direction of the Councils Medical Adviser, at these times the whole area was covered by a thin layer of clean soil to avoid contaminated dust being blown into surrounding areas in dry periods. This however was advantageous in further dilution of the contaminated material in the fill.

It was envisaged that in the long term, contaminated leachate might exit to the river via the new river wall and that there may be problems arising from corrosion of steel tie rods and raking piles forming part of the rival wall construction.

Engineering and scientific opinion based on analytical data, and extensive tests carried out earlier to determine the geological and hydrological character of the site discounted both possibilities. Nonetheless, heavy coatings of bituminous protection were applied to tie rods in the consolidated backing to the main river wall construction.

The backing of heavily consolidated material and the steel sheet piling plus reinforced concrete structure of the river wall taken down to the base of natural hard chalk is

TABLE 1

	Licence Limit	Mean	Total
Cadmium	20	1.07	200
Copper	1500	532.20	200
Mercury	10	1.46	200
Nickel	1000	85.70	200
Lead	2000	877.80	200
Zinc	2000	870.70	200
Cyanide	100	2.98	200
Toluene Extract	1%	0.24%	200
Sulphide	250	2.64	200
Thiocyanate	200	50.00	6
Ferri-Ferro Cyanide	2000	100.00	6
Arsenic	150	20.29	200

Unless otherwise stated, all results are expressed as parts per million, i.e mg/kg dry soil. Please note, 6 samples only were analysed for Thiocyanate and Ferri-Ferro Cyanide because total cyanide determinations produced only 6 results sufficiently significant to warrant analysis for complexed cyanides (3).

considered virtually impermeable to leachate.

RESULTS

When facility 4J/4K was completely filled, a cover of soil was placed overall and seeded to provide a temporary surface pending surcharging of the site to accelerate consolidation. Prior to this, the site was subject to investigation as if it were a parcel of newly acquired land with a potential contamination problem. The object of this was twofold; the first to determine the general level of contamination in the body of the site in order to assess the effectiveness of disposal control procedures, the second being to aid the more important evaluation of the long term health hazards of the facility with a view to its eventual development as housing land. Additionally, boreholes were sunk through the fill to investigate the possibility of methane gas being generated in residual organic matter in the remaining river silt at the base of the facility.

Effectiveness of disposal methods.

The procedures for control of disposal in 4J/4K and the specified compaction methods had a diluting effect on the fill which had not been anticipated. Within a selected group of contaminants comparison of the mean values calculated from the analytical data with the limits imposed by the disposal licence indicates (so far as such comparisons are valid) a very satisfactory outcome which also served to highlight the possibility of using traditional civil engineering techniques for in-situ rehabilition of contaminated land.

A comparative table showing mean values for contaminants within the site and licence limits is set out in Table 1. Twenty five trial pits were dug to a depth of 6.00m and samples taken at 0.15, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00 m below the surface producing 200 samples in all.

Disposal site into housing land

The transition of 4J/4K into housing land was accomplished with far less difficulty than was thought possible when the project was embarked upon. The overall level of pollution was found to be such as to require much less remedial work than those sites from which the material had been removed in the first instance. In consequence, it was recommended that only 0.50 metres of clean imported capping material be placed over the whole site to make it suitable for housing development.

The site will be subjected to re-investigation when the final layout of the housing is known and regular monitoring will be undertaken over a period of 5 years after building is completed. This procedure is not peculiar to 4J/4K, but is part of an overall monitoring policy for Thamesmead agreed with the local authority.

Several years will elapse between completion of the disposal area filling and its redevelopment for housing purposes. Monitoring is expected to reinforce experience elsewhere at Thamesmead which has shown that vertical upward migration of contaminants via barrier layers does not take place. Additionally, the depth of cover will be augmented as necessary to avoid disturbance by householders.

The value of the exercise in financial terms is probably impossible to quantify due to the influence of changing land values at Thamesmead attributable to other factors, but it is known that actual cost savings in creating new land out of re-cycled, valueless material will not be less than £5 million. The true worth of the asset has also been much enhanced by the knowledge gained in creating it, in that it has been found that major disturbance and localised re-distribution of contaminated material on two other major sites has lead to significant reductions in the level of remedial works needed to make them safe.

ACKNOWLEDGEMENTS

The officers of the 'Inter Departmental Assessment Panel on Contaminated Land' of the Greater London Council. A uniquely experienced body of people now disbanded since the abolition of the G.L.C.

REFERENCES

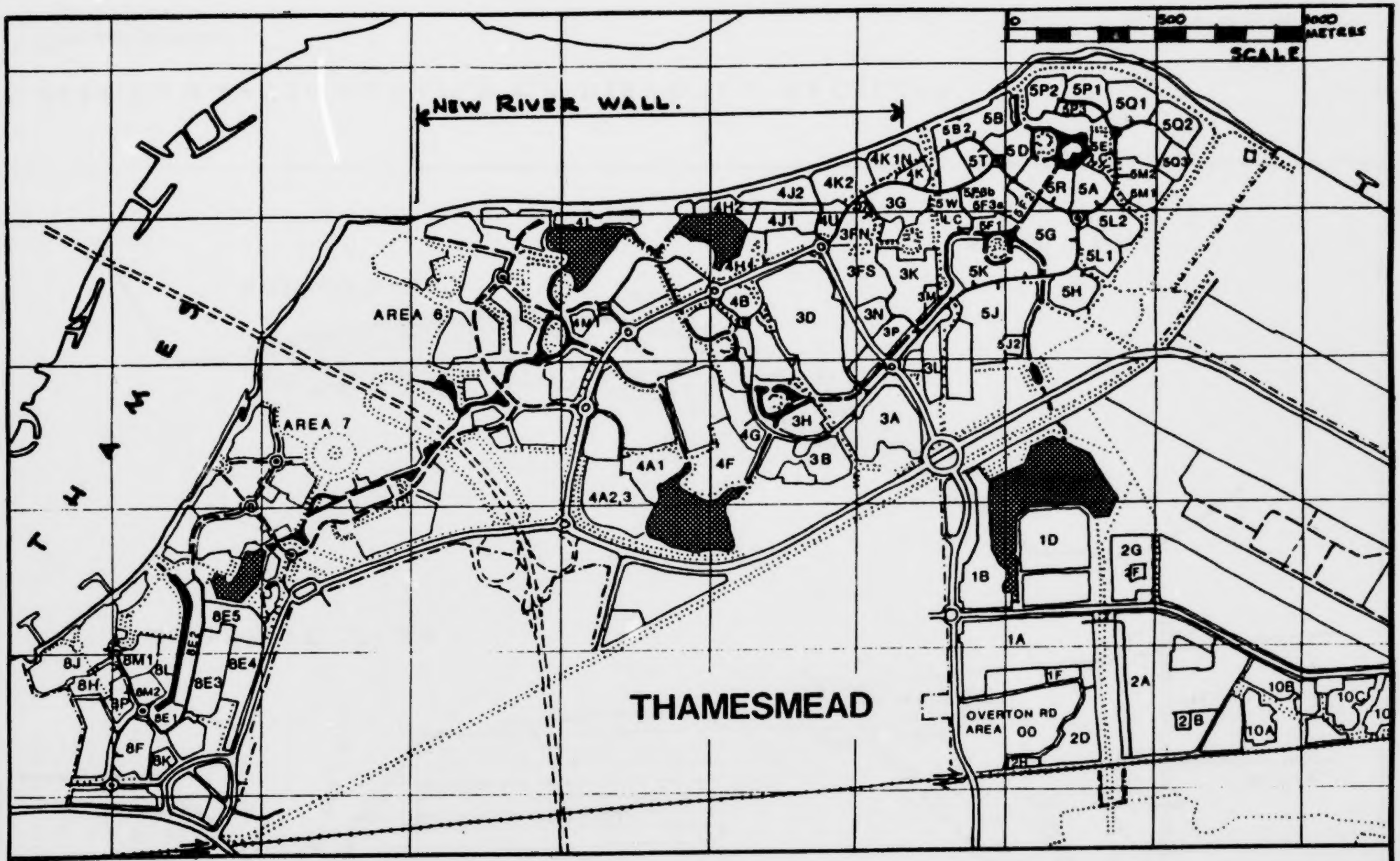
1. Taylor G. and Lennon A., 'The disposal of wastes arising from the development of contaminated land'.
London Waste Regulation Authority. North Block, The County Hall London SE1 7PB. U.K.

2. Lowe G.W. Investigation of Land at Thamesmead and assesment of remedial works to bring contaminated land into beneficial use. London Scientific Services, Room 629, The County Hall, London SE1 7PB U.K.

3. Carpenter R.J. A laboratory report: Investigation into potential contamination at Thamesmead Area 4J/4K. for the G.L.C., London Scientific Services, Room 629, The County Hall, London SE1 7PB. U.K.

Disclaimer

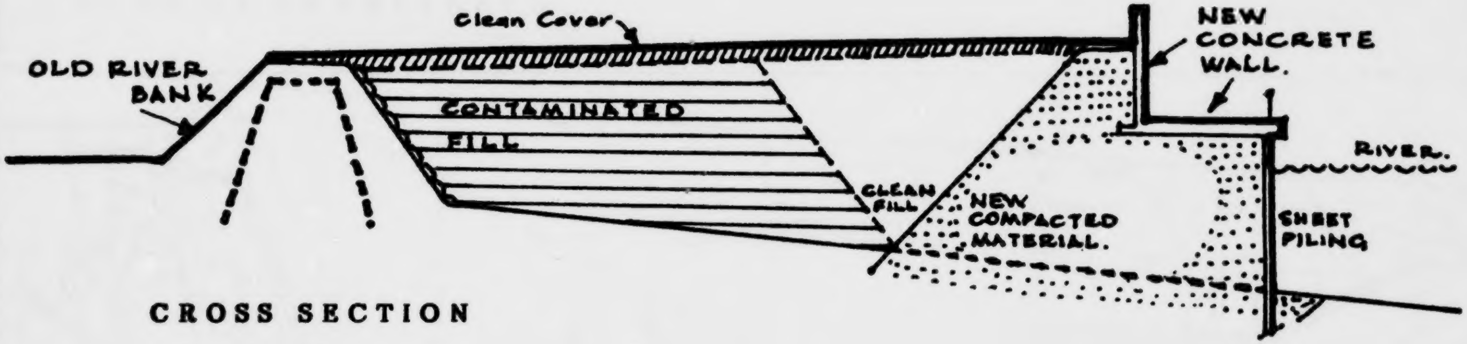
The work in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.


0
500
1000 METRES
SCALE
NEW RIVER WALL.
THAMES
THAMESMEAD
AREA 6
AREA 7
OVERTON RD AREA 00
5P2
5P1
5Q1
5Q2
5Q3
5B
5B2
5D
5T
5R
5A
5M2
5M1
5L2
5L1
5G
5K
5J
5J2
5H
5W
5F1
4K1N
4K
4K2
4J2
4J1
4H2
4H1
4L
4M
4U
4B
4G
4F
4A1
4A2,3
3G
3FN
3FS
3K
3M
3N
3P
3D
3L
3A
3H
3B
1D
1B
1A
1F
2G
2F
2A
2B
2D
2H
10A
10B
10C
8E5
8E4
8E3
8E2
8E1
8J
8H
8M1
8M2
8L
8P
8F
8K

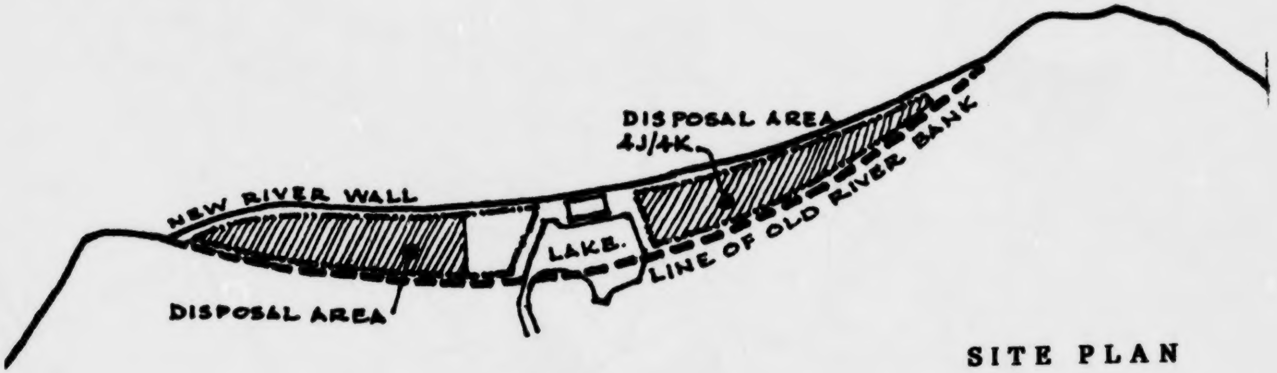
PLAN OF THAMESMEAD

Layout of Housing Areas

DIAGRAM 1


Clean Cover
OLD RIVER BANK
CONTAMINATED FILL
CLEAN FILL
NEW COMPACTED MATERIAL.
NEW CONCRETE WALL.
RIVER.
SHEET PILING

CROSS SECTION


NEW RIVER WALL
DISPOSAL AREA
LAKE.
DISPOSAL AREA 4J/4K
LINE OF OLD RIVER BANK

SITE PLAN

DIAGRAMMATIC DETAILS OF DISPOSAL FACILITY

Plan and Section

DIAGRAM 2

SECURE LANDFILL DESIGN/OPERATION
TO REDUCE LEACHATE AND CLOSURE COST

Randolph W. Rakoczynski, P.E.
Waste Resource Associates, Inc.
2576 Seneca Avenue
Niagara Falls, NY 14305

ABSTRACT

As permitting delays and increasing capital construction costs force facility developers to consider landfill cells of increasingly larger proportions, the tremendous volumes of leachate generated by these larger facilities act to limit their size drastically. The "central low point" design and method of operation which is presented allows these larger facilities to be constructed and operated economically. Volumes of leachate produced during the operating life of a central low point facility are reduced by as much as 90-95% when compared with leachate production using conventional landfill designs. Additionally, the central low point design also allows the cost of closure funding to be reduced by as much as 90-95%.

INTRODUCTION

As environmental regulations governing the management of hazardous waste have begun to focus more closely on landfill facilities, engineering design and methods of operation for these facilities have been forced to change. What may have been standard operating procedures a few years ago are now out-moded methods which no longer meet the minimum regulatory requirements.

The Hazardous and Solid Waste Amendments of 1984 (HSWA) and the minimum technology requirements for land disposal facilities this statute has imposed have further forced facility developers to carefully reconsider their plans and designs. The minimum technology design requirements along with the costs associated with closure and post-closure of these facilities and the unavailability of non-sudden environmental impairment liability coverage has all but stalled the development of any new landfill disposal facilities.

PURPOSE

In an attempt to stimulate the development of the new facilities which will be needed in order to properly handle future volumes of industrial hazardous waste generation and the residuals from "high technology" treatment processes as well as the enormous volumes of contaminated residues from Superfund remedial action clean-ups and surface impoundment closures, a landfill design which cost-effectively meets the minimum technology requirements of HSWA has been formulated.

In addition to meeting minimum technical design requirements, the landfill design incorporates certain economies of scale and other economic incentives attractive to prospective new facility developers. Since the design enables much larger tracts of acreage to be developed, it avoids the costly permitting delays inherent in the sequential development of individual landfill cells which are much smaller in size but when completed provide the identical total capacity of the larger cell.

APPROACH

In developing larger tracts of acreage into a landfill facility, the design engineer is constrained by the fact that as the landfill acreage is increased, the volumes of leachate produced from the accumulation of rainfall also increase. Oftentimes the increased volumes of leachate associated with larger landfills and the costs involved with removing and treating those volumes exceeds the savings realized in the economies of scale provided by construction of larger facilities. The design to be presented here circumvents the problems of excess leachate generation by larger landfills with straight-forward, common sense principles which are uniquely and innovatively incorporated into the design and operation of the facility.

The initial step in the engineering design of any landfill disposal facility is to maximize the disposal capacity of the proposed facility over the acreage intended to be developed. The primary constraints in maximizing the capacity are usually the depth to the seasonally-high water table and the maximum height above grade which local and/or state environmental regulatory agencies will permit for the proposed facility. The desire to maximize disposal facility capacity has in the past led the design engineer to locate the bottom "floor" of the landfill the required distance from the seasonally-high water table with minimal slopes on the bottom floor (usually 1 percent-2 percent) to promote drainage and leachate collection. If slopes on the bottom of the landfill are however increased to on the order of approximately 2-5 percent and the floor is contoured to a centrally-located, common low point, the landfill facility can be designed and operated to reduce the costs associated with leachate removal/treatment and closure of the facility.

Liner System

The liner system employed in the proposed landfill facility design conforms to the minimum technology requirements put forth by EPA as a result of HSWA. Starting from the bottom of the liner system, the liner system is composed of the following components:

- three (3) feet of recompacted low permeability soil liner (upper portion of this layer is processed to remove stones and other foreign debris);

- flexible membrane liner (FML) of 30 mil high density polyethylene (HDPE);
- one (1) foot of granular material (secondary leachate collection and/or leak detection zone);
- flexible membrane liner (FML) of 80 mil high density polyethylene (HDPE);
- one (1) foot of granular material (primary leachate collection zone);
- geotextile fabric (for filtration of leachate).

Limiting Active Disposal Area

In order to minimize the amount of rainfall which is accumulated as leachate, the active area of the landfill facility must be confined to an area surrounding the common low point. An access roadway can be constructed so that heavy equipment which will be used to deposit waste transferred from receiving facilities can easily place waste in the active disposal area. In addition to providing access for heavy equipment, the roadway also serves as the base of a segregation berm(s) which separates the landfill facility into individual cells which can each be used to dispose of specific wastes that would be incompatible if disposed of together. The placement of additional berms or separations within the individual cells allows uncontaminated rainfall to be kept from contacting the deposited waste.

Waste Placement

Conventional waste placement procedures involve depositing waste in lifts across the entire floor of the landfill facility. Once a horizontal lift is completed, the next lift is begun. This method of waste placement has two major drawbacks; first the entire surface area of the floor of the landfill is subject to leachate generation and secondly, closure of the facility cannot begin until the entire capacity of the landfill facility is consumed.

In the common low point design, waste placement is relegated initially only to the active disposal area surrounding the low point. Once the elevation of the waste reaches the level of the access roadway/segregation berm, the roadway is raised with the placement of additional recompacted low permeability soil. Waste placement continues from the raised roadway surface around the central low point until its elevation again reaches the road surface and the roadway level is again raised. This procedure continues until the emplaced waste and roadway reach their desired final elevations. Waste deposition continues on the inclined working face which has been created in each cell.

Progressive Partial Closure

As the bottom toe of the slope of the working face begins to approach the temporary rainwater/leachate separation berm or device, the installation of the final closure cap in those areas that have reached final waste elevation can proceed. The components which comprise the final closure cap are from bottom to top:

- one (1) foot of intermediate cover soil;
- two (2) feet of recompacted low permeability soil;
- geotextile fabric;
- flexible membrane liner (FML) of 80 mil high density polyethylene (HDPE);
- geotextile fabric;
- two and one-half (2 1/2) feet of soil;
- one-half (1/2) foot of topsoil;
- vegetation.

As the installation of the final closure cap is nearing completion in those areas where emplaced waste elevations have reached desired levels, the temporary rainwater/leachate separation berm or device is moved further outward from the central low point so that waste deposition on the inclined working face can continue.

PROBLEMS ENCOUNTERED

In formulating the design, the following problem areas were identified and addressed:

- emplaced waste stability
- installation of secondary leachate or leak detection zone (LDZ) on internal side slopes of landfill perimeter
- access to the inclined working face over the final closure cap
- drainage of stormwater from the final closure cap
- identification of the source of any leaks detected in the secondary leachate collection zone.

Each of the problem areas was resolved as follows:

Waste Stability

In order to insure stability of the final upper surface of waste for final closure cap placement and heavy equipment access, it was determined emplaced waste had to meet certain criteria. A minimum angle of cohesion and load bearing capacity must be provided. As part of inbound quality control testing, a minimum unconfined compressive strength and absence of "free liquid" must be confirmed for wastes to be deposited directly into the active disposal areas. If either "free liquid" is present or insufficient load bearing capacity is provided, the waste must be pre-treated using appropriate chemical fixation/solidification agents.

Sideslope LDZ

The granular material used in the secondary leachate removal or leak detection zone cannot be placed on the angle required for the internal sideslopes of the landfill facility. Along the internal landfill sideslopes, the granular material was replaced with a drainage net fabricated of high density polyethylene.

Working Face Access

In order to allow heavy equipment continued access to the working face for waste deposition, a temporary roadway must be provided over the final closure cap.

Closure Cap Drainage

Drainage conduits (clay tile) are provided to direct closure cap stormwater run-off to collection channels around the landfill perimeter.

Leak Identification

Inherent in the design is the shortcoming that if the primary or upper FML should leak and liquid is detected in the secondary leachate collection or leak detection zone, the source of that leak cannot be accurately identified. In a large landfill facility of significant acreage this represents a problem with regard to any attempt to undertake remedial action to repair the primary or upper FML. A leak detection and identification system has been provided in this central low point design. A matrix of electrical probes are placed within the granular material that comprises the secondary leachate collection or leak detection zone. These probes are monitored so that if a leak occurs and leachate enters the zone, the origin of that leak can be identified.

RESULTS

The most important benefit resulting from the landfill design presented is the dramatic reduction in both leachate generated during the operating life of the facility and the volumes of leachate which must be withdrawn following the completion of closure. In conventional landfill design and operation, completely dewatering a closed landfill may extend many years into the post-closure care period of the facility. Until the closed facility is completely dewatered, a head of leachate exists within the landfill which can potentially be a driving force for contaminant migration in the event of any liner deterioration or failure. The landfill design and method of operation which is proposed are successful in limiting operational and post-closure leachate production because;

- active disposal area within the facility is limited during the operating life;
- deposited waste leachate generation is limited primarily to the active working face which is inclined and minimizes percolation of rainfall down into the waste;
- final closure cap is progressively installed in increments which eliminates percolation of rainfall into the waste;
- bottom floor of the landfill has steeper slopes which improve leachate collection efficiency.

The economic analysis which follows demonstrates the cost savings realized with use of the proposed design/method of operation versus use of conventional secure landfill design/ operational methods.

Economic Analysis

The following table presents a

comparison of disposal capacity for a conventional "flat" bottom design and the "central low point" design for a landfill which is 30-feet deep. The "flat" bottom design assumes floor slopes on the order of 1-2 percent. The "central low point" design assumes floor slopes of on the order of 2-5 percent. No mounding of the final closure cap of the facility has been considered in computing the disposal capacities listed, since the extent to which mounding is allowed varies considerably from state to state.

Landfill Size (acres)	Disposal Capacity (cubic yards)	
	"Flat"	"Central Low Point"
5.0	206,000	181,000
10.0	411,000	342,000
15.0	630,000	482,000
20.0	817,000	604,000
30.0	1,250,000	796,000
40.0	1,650,000	935,000
50.0	1,945,000	1,028,000

In order to compute the leachate production volumes which are presented in the following table, a 30-inch net annual rainfall minus evaporation was used. It was assumed that this net annual rainfall was responsible for leachate generation over the intended operating life of the facility. The operating life was computed by dividing disposal capacity by a uniform annual waste receipt volume of 100,000 cubic yards.

Landfill Size (acres)	Leachate Production (millions of gallons)	
	"Flat"	"Central Low Point"
5.0	8.4	0.7
10.0	33.5	2.8
15.0	77.0	5.9
20.0	133.7	9.9
30.0	305.7	19.5
40.0	538.0	30.5
50.0	794.7	41.9

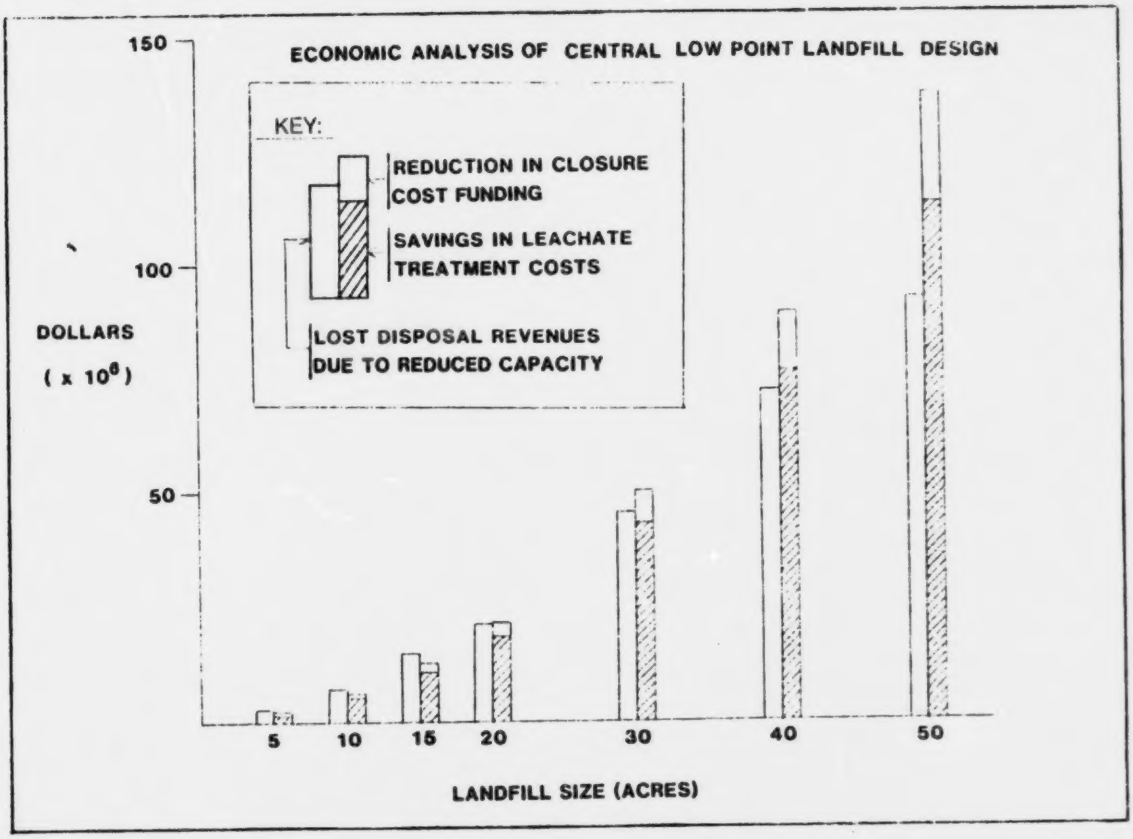
In computing leachate production volumes for the "central low point" design, it was assumed that only one-tenth of the landfill surface area would be in active use at any point in time during the operating life of the facility.

Landfill Size (acres)	Closure Cost (millions of dollars)	
	"Flat"	"Central Low Point"
5.0	$0.5	$0.05
10.0	$1.1	$0.1
15.0	$2.1	$0.2
20.0	$3.3	$0.3
30.0	$7.4	$0.5
40.0	$13.8	$0.8
50.0	$24.1	$1.0

The above closure cost comparison was computed based on closure financial mechanism for assuring closure must be in-place prior to facility start-up, the closure costs presented reflect a 10% escalation factor over the full term of the operating life of the facility.

This escalation factor accounts for the return on the closure fund dollars which the facility owner/operator would realize if those dollars were not tied up in the closure funding. The closure cost funding for the "central low point" design assumes closure of the maximum one-tenth of landfill surface area which is in active use at any point in time.

By comparing the lost disposal capacity for the "central low point" design (valued at $100 per cubic yard) with the savings in the costs for removing/treating leachate (estimated at $0.15 per gallon) and the reduction in closure cost funding, the following graph shows clearly that as the acreage of a proposed facility begins to exceed 20 acres the "central low point" design is justified in lieu of the conventional "flat" bottom design.



ACKNOWLEDGEMENTS

The "central low point" design is protected under a U.S. patent which was recently issued and was developed in conjunction with a Part B Application compiled and submitted on behalf of Sechan Limestone Industries, Inc. (Portersville, PA).

John I. Rolfe, P.E. (Pegasus Consultants, Niagara Falls, NY) collaborated on certain selected portions of the design.

The leak detection system for the central low point design was developed by Electronetics Corporation (Clarence, NY) and is protected under a patent which is pending. Waste Resource Associates, Inc. is the sole agent responsible for the licensing of the rights to use the leak detection system.

Disclaimer

The work in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

SAFE, ZERO-MIGRATION ULTIMATE DISPOSAL OF SOLID HAZARDOUS WASTE IN SALT CAVERNS

H.-J. Schneider *
W. Bishop **

1 Introduction

Waste has until now been regarded as an unavoidable side effect of industrial production. Every production process, be it raw materials exploitation, basic materials production, or product manufacturing is associated with waste production. Furthermore, the consumption of the product itself also produces waste. Chemico-physical treatment, incineration and/or final disposal are available for the treatment of such waste. According to the 4th Amendment to the Law on Waste Disposal of the Federal Republic of Germany /1/, priority should be placed on waste avoidance and waste recycling, with the aim of minimizing the residues for final disposal.

Despite increased efforts and interim successes in waste reduction and recycling, the current state of waste management remains characterized by waste production on a massive scale. According to research statistics from the Federal German Ministry of the Interior for the year 1983, the Federal Republic of Germany produces a volume of 260 million t/a (Fig. 1) of waste (without agricultural wastes) of which some 5 million tons are hazardous waste. Of these 5 million t/a some 10 % are incinerated, 25 % are exported to be landfilled generally, 30 % are detoxified and 35 % landfilled.

---

*) Priv.-Doz. Dr.-Ing. Dipl.-Geol. Hans-Joachim Schneider
KAVERNEN BAU- UND BETRIEBS-GMBH
Roscherstraße 7, D-3000 Hannover 1
**) W. Bishop, Vice President, Engineering
PB-KBB Inc.
P.O.Box 19672, Houston/Texas 77024, U.S.A.

To teckle this problem, the law mentioned previously, prescribed technical and organizational regulations designed to ensure maximized environmental waste treatment and disposal.

For waste disposal, this entails continual improvement of concepts and methods with the aim of avoiding the errors of the past which led to the creation of the current abandoned site problem.

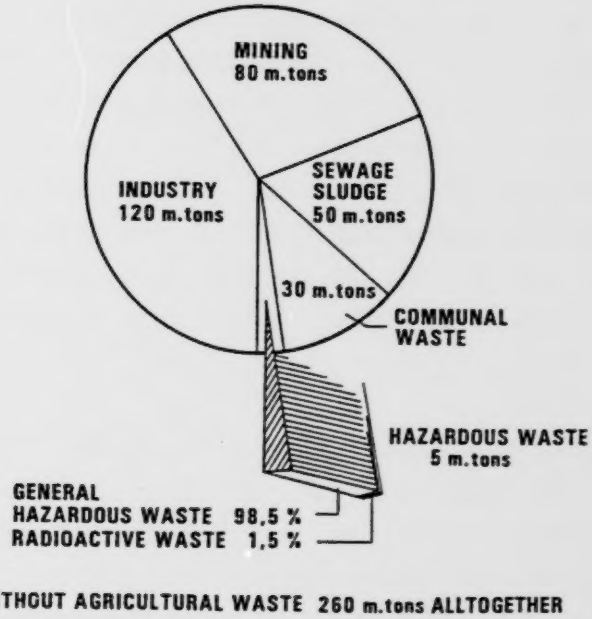


Fig. 1

Annual waste production in the Federal Republic of Germany (source: Federal Ministry of the Interior, 1983)

2 Ultimate disposal of hazardous waste

With reference to the current state of engineering the ultimate disposal of waste should ensure complete isolation of the dangerous materials. The environmental hazardous waste treatment is quite insufficiently developed in many industrial countries, according to THOMANETZ /2/. The following items are regarded as the major critical aspects:

- landfill disposal of all types of hazardous waste without prior systematic waste selection
- the treatment of highly water soluble waste or waste particles in water suspension in the sewage system
- off-shore dumping of all types of hazardous waste
- exporting hazardous waste.

To reduce the problems associated with landfill disposal, largely involving seepage water, long-term safety and follow-up costs, DRESCHER /3/ proposes the strict separation of waste flows. Accordingly, only detoxified, fixable and/or degradable waste may be landfilled, whereas all toxic, non-conditionable and water soluble wastes are to be finally deposited in underground repositories (Fig. 2).

In contrast with landfill concepts, underground repositories in deep salt formations are based on natural geological barriers which, due to their impermeability and distance to aquifers, ensure effective isolation from the biosphere (Fig. 3).

Highly toxic, non-pyrolysable waste is currently deposited in the Herfa Neurode salt mine repository /4/. The large amounts of hazardous waste to be deposited in future as a result of clean air regulations call for a more economical underground repository concept with higher capacities for bulk wastes. Plans are now being developed to meet those requirements by disposal in salt caverns.

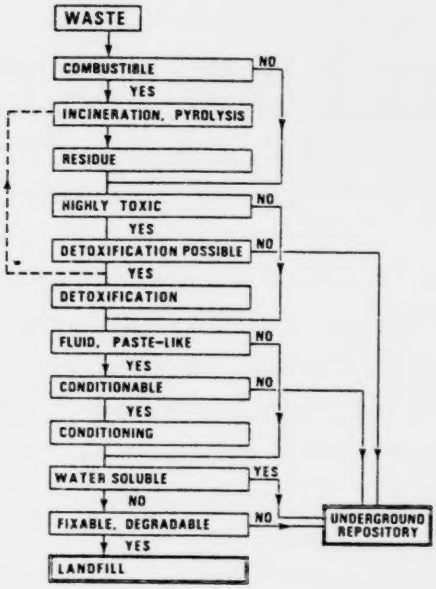

WASTE
COMBUSTIBLE
NO
YES
INCINERATION, PYROLYSIS
RESIDUE
HIGHLY TOXIC
NO
YES
DETOXIFICATION POSSIBLE
NO
YES
DETOXIFICATION
FLUID, PASTE-LIKE
NO
YES
CONDITIONABLE
NO
YES
CONDITIONING
WATER SOLUBLE
YES
NO
FIXABLE, DEGRADABLE
NO
YES
LANDFILL
UNDERGROUND REPOSITORY

Fig. 2

Waste treatment flow chart for hazardous waste
(according to DRESCHER /3/)

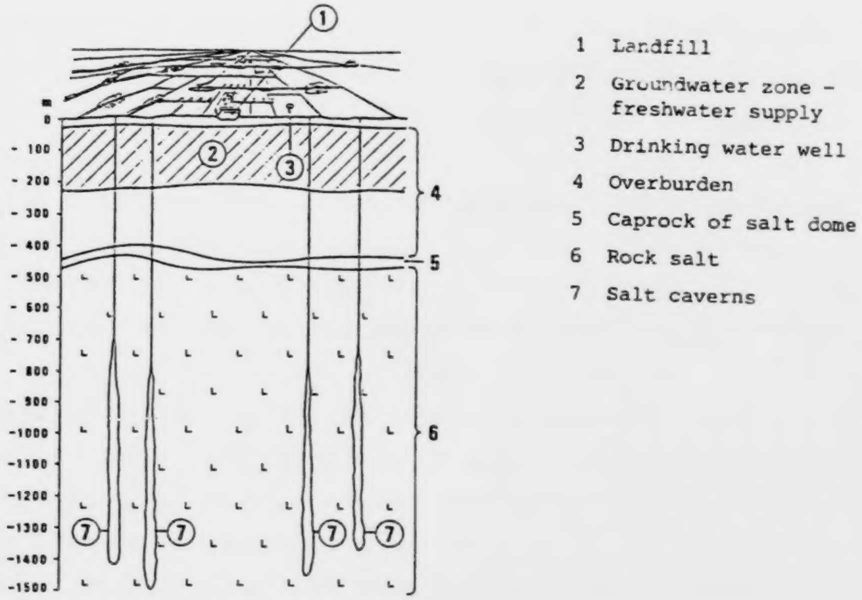

m
0
- 100
- 200
- 300
- 400
- 500
- 600
- 700
- 800
- 900
-1000
-1100
-1200
-1300
-1400
-1500
①
②
③
4
5
6
⑦
1 Landfill
2 Groundwater zone - freshwater supply
3 Drinking water well
4 Overburden
5 Caprock of salt dome
6 Rock salt
7 Salt caverns

Fig. 3

Position of surface waste disposal and salt
cavern repository in relation to the ecosystem

3 Barrier concepts

The underlying principle of hazardous waste containment is the shielding of the environment against toxic materials by use of artificial or natural barriers. Because of the geochemical complexity of hazardous wastes (HERRMANN, et al /5/), this may not be simply understood as the effective sealing of the repository to prevent toxic material migration into the environment. The influence of the atmosphere and geosphere upon the deposited wastes as well as the interactive chemical reactions between the chemicals themselves must be taken into account (GÖTTNER /6/). Reactions in landfills are supported by groundwater (mobile phase) which will bring different types of waste together by acting as a solvent. This could lead to the formation of new toxic materials against which the barriers were not designed and consequently to the uncontrolled release of toxic materials. Typical reactions are formations of soluble complexes with toxic anions and heavy metals, resulting in mobilization of both. Some organic compounds may permeate through hydrocarbon-based foil seals.

These criteria placed on the barrier concept require the consequent realization that one should not depend on a single barrier in order to shield the environment effectively. A number of safety systems or multibarriers must be integrated.

In the case of landfills such a multibarrier system is designed around the following individual parameters (STIEF, 1986 /7/):

- landfill location
- landfill base sealing system
- landfill shape and dimensioning
- surface seals
- usage
- post treatment, controllability and repairability of the barriers

The individual barriers of an underground repository consist of:

- host rock
- distance to surface and aquifers
- lining and sealing system
- sealing bulkheads
- waste conditioning
- emplacement
- access system to underground cavity as well as
- control possibilities and post treatment.

Disposal concepts for the ultimate disposal of hazardous waste which ensure the maximum long-term safety and minimum post treatment measures must be selected in the interest of future generations. Underground waste disposal represents the only solution for numerous types of waste.

Salt formations, i.e. rock salt deposits possess several characteristics that qualify it as the prime candidate for a hazardous waste storage medium. Salt is in its native state solid and practically impermeable. This is a favorable factor to retain the waste and also to shield it from groundwater, thus allowing the disposal of mixtures of waste rather than segregated ones.

4 Salt cavern repository

4.1 Construction of salt caverns

Salt caverns are constructed in salt formations by solution mining. The construction places certain requirements on the geological characteristics of the salt structure, such as sufficient thickness, extension above depths of 2 000 m, and relatively pure salt composition.

To construct caverns using the solution mining process, wells are sunk with standardized deep drilling techniques down to the projected final cavern depth. The last cemented casing extends some 100 to 200 m into the salt formation. Three concentric strings are installed for the actual solution mining process (Fig. 4). Freshwater or seawater is pumped into the cavern zone through the inner string. The water dissolves the salt on the walls of the cavern and the brine is extracted through the first annulus. The outer annulus is used for blanket material (i.e. oil) injection to control vertical leaching in the roof zone.

The current state of the art of solution mining engineering enables the construction of caverns of desired dimensions /8/. Echometric surveys are performed to monitor the development of the cavern shape.

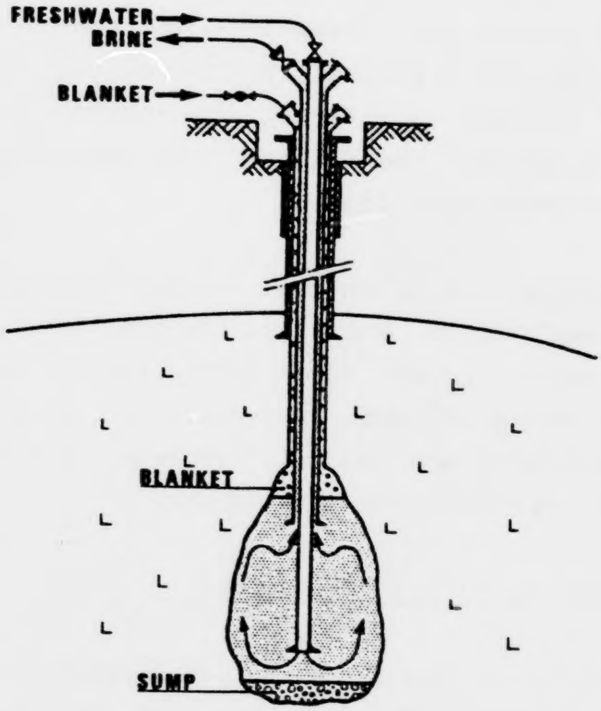


Fig. 4

Construction of salt caverns using the direct solution mining method (schematic diagram)

4.2 Geotechnical evaluation of safety of salt caverns

The evaluation of geotechnical criteria for the safety of a salt cavern repository is analogous to the criteria for evaluating oil and gas storage caverns. The stability of a cavern is determined by its position in the salt rock and by the cavern spacing in a cavern field. The distance between the caverns must be calculated such that stress interactions are minimized.

Special attention must be placed on cavern convergence or volume loss. Because of its rock mechanical properties, salt is subject to visco-plastic deformation at the pressures and temperatures encountered at these depths. A cavern repository at internal atmospheric pressure causes salt creep into the cavern with consequent volume reduction. To restrict convergence the period during which the cavern is subject to internal atmospheric pressure must be limited. In other words, the filling with waste must be completed within a reasonable time frame.

The problem of flooding has often been raised in the context of final deposition in salt mines. This problem does not exist in the case of salt cavern repositories, since salt caverns are completely packed with waste after filling. Moreover, the access well will be completely back-filled and sealed, thereby cutting off all escape routes to the overburden or atmosphere.

4.3 Salt cavern repository operation

Before waste is deposited the brine-filled cavern is evacuated by use of submersible pumps. The waste is fed into the cavern via the access well. It will be continuously delivered at an projected annual rate of 100 000 - 200 000 m^3 down an additional string hung in the well. This string protects the outer casing against corrosion and abrasion and can be pulled out and/or replaced in event of damage.

Suitable methods for emplacement are gravity-fall or pump-driven slurry delivery. For gravity-fall filling, the waste must be conditioned, i.e. solidified and classified, so that on one hand it meets the specific gravity-fall dumping characteristics and on the other, reactions between wastes in the cavern are prevented. In the case of pump-driven slurry dumping, additives are used for in-situ solidification.

4.4 Post operational phase

After complete filling of the cavern with waste, the cavern must be permanently sealed against the biosphere. For this purpose the open borehole above the cavern roof and the whole length of the cased well are filled with cement, clay and bitumen. The surface site is recultivated and returned to its original use. Post treatment and long-term monitoring of the cavern repository are not necessary, since the waste is virtually permanently (i.e. for geological periods), isolated from the environment through the geological barrier and the well plug. The complete back-filling of the cavern precludes any problems relating to stability and convergence.

5 Summary

Salt cavern repositories represent a significant addition not only to landfills but also to mined underground repositories. Highly water soluble hazardous waste, which commonly contaminates seepage waters of landfills, can be deposited in salt caverns under zero-migration conditions.

The operation of salt cavern repositories without underground staff and the high disposal capacity render salt cavern repositories economically and environmentally suitable for the disposal of bulk waste. Although, highly toxic waste with recycling potential should continue to be deposited in mined repositories.

REFERENCES:

/1/ Gesetz über die Vermeidung und Entsorgung von Sonderabfällen (Abfg). Bundesgesetzblatt, Jahrg. 1986, Teil 1.

/2/ Thomanetz, E. (1986): Ansätze zur umweltgerechten Sonderabfallentsorgung, dargestellt an ausgewählten Beispielen. Müll und Abfall, Heft 8, S. 312 - 316.

/3/ Drescher, J. (1985): Ingenieurgeologische Aspekte bei der Sonderabfallablagerung. Ber. 5. Nat. Tag. Ing.-Geol., Kiel 1985, S. 57 - 67

/4/ UTD: Untertagedeponie Herfa-Neurode. Firmenbroschüre, Kali und Salz AG, Kassel, S. 16

/5/ Herrmann, A.G.; Brumsack, H.J. & Heinrichs, H. (1985): Notwendigkeit, Möglichkeiten und Grenzen der Untergrunddeponie anthropogener Schadstoffe. - Naturwissenschaften 72, S. 408 - 418.

/6/ Göttner, I.J. (1985): Mögliche Reaktionen in einer Sonderabfalldeponie - Folgerungen für das Deponierungskonzept. Müll und Abfall, Heft 2, S. 29 - 32.

/7/ Stief, K. (1986): Das Multibarrierenkonzept als Grundlage von Planung, Bau, Betrieb und Nachsorge von Deponien. Müll und Abfall, Heft 1, S. 15 - 20.

/8/ Quast, P. und Beckel, S.: Derzeitiger Stand der soltechnischen Planung von Speicherkavernen im Salz und die damit erzielten praktischen Ergebnisse. Erdöl-Erdgas-Zeitschrift (1981), H. 6, Jg. 97, S. 213 - 217

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

IN SITU TREATMENT PROCESS FOR REMOVAL OF VOLATILE HYDROCARBONS FROM SOILS: RESULTS OF PROTOTYPE TEST

Phillip N. La Mori
Vice President and Technical Director

Michael Ridosh
Vice President

TOXIC TREATMENTS (USA) INC.
901 Mariner's Island Blvd.
Suite 315
San Mateo, CA 94404

ABSTRACT

This paper reviews the capabilities of a new in situ remediation technique for soils contaminated by volatile hydrocarbons and presents the results of the prototype test. The technique uses two overlapping drills 5 feet in diameter to dispense heat in the form of steam and hot air into the soil to depths of 30 feet to volatilize hydrocarbons. The drills thoroughly mix and pulverize the soil. The escaping hydrocarbon gas vapors are contained and captured in a surface shroud and then condensed and removed from the air in an above ground closed-loop system. The cleaned air is compressed and returned to the drills. We have treated 4,700 cubic yards of soil in a prototype test, reducing petroleum hydrocarbon from 39,000 ppm to below 100 ppm in the best case. The average reduction was 91.4% to 191 ppm. A redesigned system is currently remediating a chlorinated hydrocarbon site (concentrations to 8900 ppm) and the results of this work will be given at the meeting.

INTRODUCTION

The objective of this paper is to review the capabilities of a new in situ remediation technique for soils contaminated by volatile hydrocarbons and present the results of a site remediation.

Treatment of wastes and contaminated soils can be accomplished via off-site or on-site treatment of the excavated materials or by in situ treatment. In situ treatment offers the following advantages:

- Eliminates the public health, safety and environmental risks which are associated with excavation, transportation, storage and handling of hazardous materials.
- Does not require additional land areas for treatment.
- Soil is left in place prior to, during and after treatment.
- The process is more acceptable to the community due to low noise, traffic, visual impact and emissions.
- Liability for off-site handling or disposal areas is eliminated.

There are major limitations and concerns associated with remediation approaches which rely on the use of liners, caps, slurry walls, grout curtains, etc., for waste containment and those which involve waste excavation and redisposal. Some of these concerns are:

- Uncertainty regarding the long-term effectiveness of the available containment technologies.
- Exposure of workers, the general public and the environment to additional risks associated with site excavation, transportation, and redisposal.
- Growing scarcity of approved off-site facilities for waste redisposal.
- The high cost of and the increasing public opposition to schemes involving waste relocation.
- Increasing criticism of on-site waste isolation and/or waste relocation at off-site facilities as shortsighted strategies that merely transfer the problem to future generations or to new locations.

The technology described here has been used for in situ soil decontamination using steam and hot air stripping and chemical oxidization of volatile hydrocarbons. It has the potential to treat soils contaminated by heavy metals, acid wastes, drilling fluids, coal gasification plant wastes and to act as an in situ dispenser of bioactive materials. We are actively investigating the use of the Detoxifier for these and other applications.

PURPOSE

The purpose of this paper is to describe a new in situ technique for soils remediation and present the results of the prototype test. This test was a full scale commercial remediation project on a site that was being redeveloped as a commercial office complex. The remediation was successful and permission to continue the development was subsequently granted. The results of a second project, currently in progress, will also be presented.

APPROACH

The heart of the Detoxifier technology is the "process tower" which is essentially a drilling and treatment agent dispensing system, capable of penetrating the soil/ waste medium to depths of 30 feet or more. The process tower consists of an assembly of two cutter/mixer bits connected to separate, hollow kellies. The bits overlap and rotate in opposite directions. The rotating action provides for simultaneous cutting, mixing, homogenizing and pulverizing of the soil. Treatment agents in dry, liquid, gaseous or slurry form can be conveyed through the hollow kellies and ejected through spray nozzles into the soil where they are mixed and homogenized (see enclosed figure).

The treatment of a site is on a block-by-block basis. The site to be treated is divided into rows of blocks, with the process tower being moved to an adjacent block after treatment of the previous block is completed.

The bit assembly is two overlapping cutting blades 5 feet in diameter. To cover all of the area to be treated, the drill is positioned with about 10 percent overlap of the grid blocks. With this overlap, the effective treatment volume, or a treatment block, is about 30 square feet of surface area times the number of feet of depth to be treated. Each foot of depth is equivalent to a little more than one cubic yard.

A rectangular enclosure called a shroud covers the treatment area to eliminate dust and to capture gas and vapor released during the subsurface treatment process. The captured offgas is treated in a process train and recycled through a compressor back to the process tower, then down to the treatment zone.

This closed-loop operation of the Detoxifier eliminates the release of volatile contaminants into the atmosphere. The unit processes comprising the treatment train are selected and designed based on the type and level of pollutants that are to be removed from the offgases.

In the treatment train used for hydrocarbon stripping, the offgas from the shroud which contains the exit air, steam and volatilized hydrocarbons, is condensed in a three-stage cooling system. Each cooling stage is followed by a cyclone demister. The final stage lowers the temperature of the gases to -10 deg. F. The gas stream is then passed through a bed of granulated activated carbon (GAC) for removal of any remaining hydrocarbons.

Following carbon absorption, the purified gas is compressed, reheated and recycled to the treatment zone through the two kellies in the process tower.

The hydrocarbon content of the shroud offgas is monitored continuously by a total hydrocarbon analyzer with a flame ionization detector (FID). The FID reading is used to adjust the treatment conditions, including the duration of treatment, to achieve desired treatment objectives.

The important features of the Detoxifier system, which represent significant innovations and advances for in situ treatment, are the following:

- o Delivery of the treatment agents directly to the treatment zone.
- o Thorough mixing and homogenization resulting in effective contact between the treatment agents and the contaminant.
- o Closed-loop operation.
- o Ability to use a range of treatment agents in liquid, gas, solid and slurry forms, thus providing versatility and ability to implement a range of options. These include thermal treatment, stripping of volatile organics, oxidation, reduction, precipitation, neutralization of inorganics and stabilization, solidification, fixation or biodegradation of a wide variety of contaminants.
- o The treatment system is mobile and transportable.

PROCESS DESCRIPTION

A prototype in situ Detoxifier was utilized in the summer of 1986 for remediation of a site in Los Angeles, California, under development as a light industrial and office complex. The site had previously been used as a truck terminal. During initial construction on the site, five underground tanks were uncovered. The tanks had contained gasoline and diesel fuel. Leakage from these tanks had contaminated over 4,700 cubic yards of soil. The in situ Detoxifier was selected for remediation of the site after an evaluation of alternatives because it: 1) did not require transport of hazardous materials 2) solved the waste problem as opposed to merely displacing it and 3) was an immediate solution requiring only a few months to complete.

The remediation process was initially investigated in a bench scale test using soil samples from the site. Those studies demonstrated that potassium permanganate oxidation as well as steam and hot air are effective for the removal of hydrocarbon contamination. Hence the cleanup operations at the site employed steam and hot air stripping and varying amounts of oxidation via potassium permanganate in the highly contaminated zones.

OPERATIONAL VARIABLES

The only variables associated with treatment by the Detoxifier are:

1. The speed of rotation.
2. The rate of penetration of the soil.
3. The amount of time spent on any one treatment block.
4. The number of passes of the drill blades through a contaminated zone.

The energy supplied by the steam and hot air for stripping the volatile compounds are delivered to the soil at the maximum output rate of the boiler and compressor. These values are presented in Table I.

RESULTS

The Detoxifier was effective in reducing the level of petroleum hydrocarbon compounds found in the soil at a wide range of concentrations. For example, in the northern portion of the site where initial hydrocarbon concentrations were on the order of 1,000 ppm or less, removal efficiencies of 75-90 percent were routinely achieved with operation of the unit on a 15' soil column for an average of 47 minutes without potassium permanganate addition. In the southern portion of the site where initial hydrocarbon concentrations averaged 10,000 ppm but reached 39,000 ppm, removal efficiencies of 90-95 percent were routinely achieved with operation of the unit on a 22' soil column for an average of 78 minutes. The Detoxifier system was demonstrated to be a viable alternative to the current technology used in contaminated soil remediation. Some limitations in the ability to remove the higher molecular weight, less volatile components of the diesel fuel were encountered. Table II below summarizes the treatment achieved.

PROBLEMS ENCOUNTERED

The main problem encountered was related to the prototype design of the process train and the anticipated concentration of the soil hydrocarbons. Analysis of the soil chemical samples before the project showed a maximum of 4-5000 ppm hydrocarbons. The process train was designed for

TABLE I - OPERATIONAL PARAMETERS

	Volume	Temperature	Pressure
Air	600 cu. ft./min.	400 deg. F	250 psi
Steam	3,100 lb./hr.	400 deg. F	400 psi

TABLE II

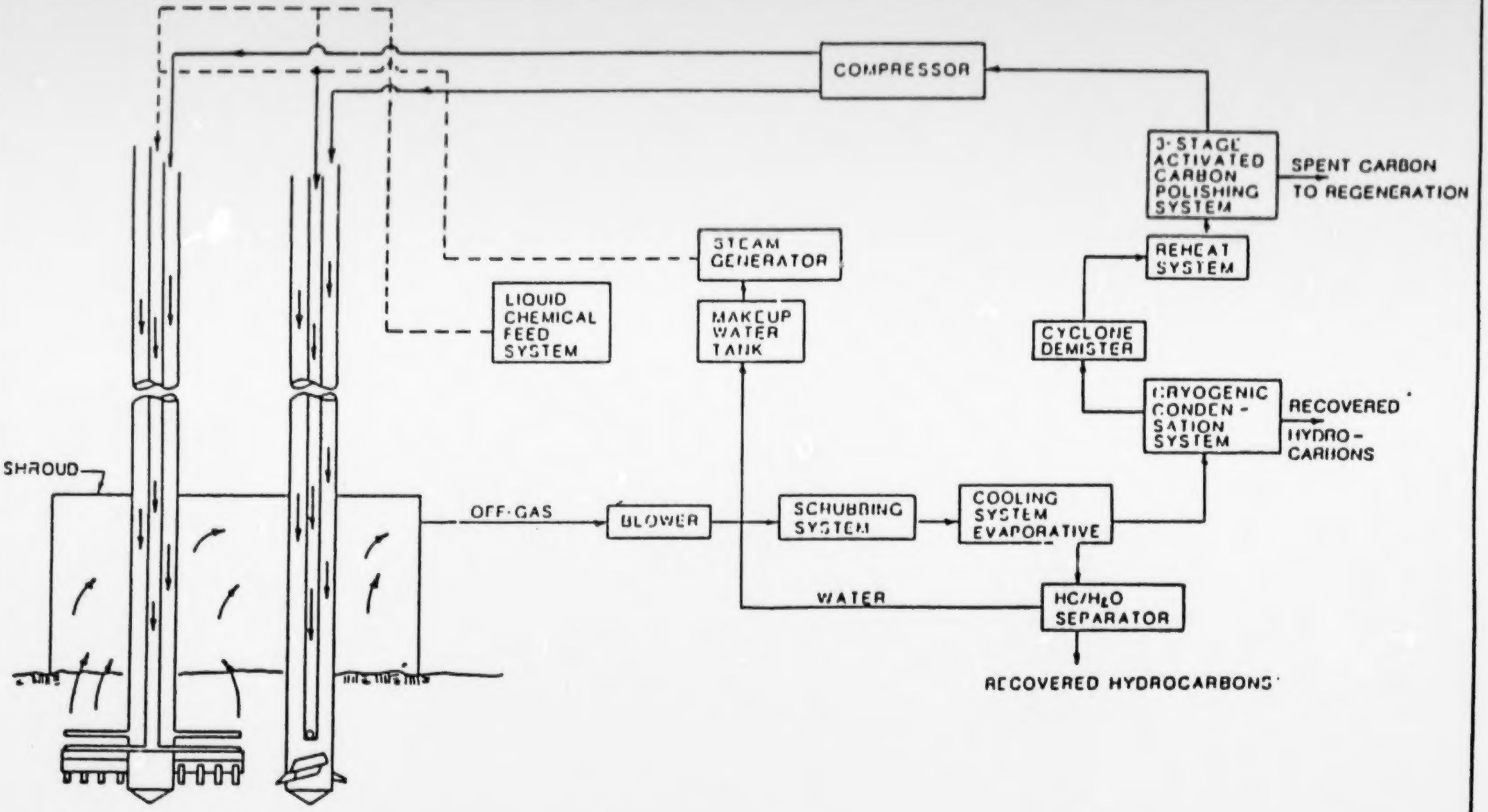
TOTAL PETROLEUM HYDROCARBONS (PPM) METHOD 418.1		
	Initial	Final
Mean	2222.5	191.4
S.D.	6059.0	301.8
Maximum	35,980	2170
%Reduction = 91.4%		

this level. In one area of the site, the actual concentration proved to be much higher, up to 39,000 ppm. This caused problems with the operation, resulting in overloading of the carbon filters and recycling of hydrocarbons into the soil. When this occurred, the soil cleanup criteria were difficult to meet. However, when the system was operating within design parameters, the soil cleanup levels were readily achieved. The process train has been redesigned to handle over 100,000 ppm initial hydrocarbon concentration in the soil. The operating procedures can be adjusted to alleviate overloading of the process train so that the current unit can remediate any type or concentration of hydrocarbon contaminated in soil.

The results of the prototype test were used to significantly modify the Detoxifier process train and process tower. The major problem found with the prototype consisted of ineffective condensation of the volatile petroleum hydrocarbons which resulted in overloading the granulated activated carbon (GAC) filter. This resulted in recycling of hydrocarbon gases and frequent changes of the GAC, decreasing treatment efficiencies. A modified Detoxifier has been built and is being used for remediation of a volatile chlorinated hydrocarbon site. Results from this project will be presented at the meeting.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.


COMPRESSOR
3-STAGE ACTIVATED CARBON POLISHING SYSTEM
SPENT CARBON TO REGENERATION
STEAM GENERATOR
REHEAT SYSTEM
LIQUID CHEMICAL FEED SYSTEM
MAKEUP WATER TANK
CYCLONE DEMISTER
CRYOGENIC CONDEN-SATION SYSTEM
RECOVERED HYDRO-CARBONS
SHROUD
OFF-GAS
BLOWER
SCRUBBING SYSTEM
COOLING SYSTEM EVAPORATIVE
WATER
HC/H2O SEPARATOR
RECOVERED HYDROCARBONS

PROCESS DIAGRAM FOR DETOXIFIER II

THE ONE-STEP METHOD FOR RECOVERY AND REUSE OF WASTE CHROMIUM FROM ELECTROPLATING PLANTS

BY

YANCEY CHOU

SHANGHI, THE PEOPLE'S REPUBLIC OF CHINA

ABSTRACT

This industrial pollution control method is applicable to the recovery of chromium chemicals from electroplating waste effluents and sludges from treating electroplating wastewaters. Through this method, the materials can be recovered and reused to make all sorts of chromium products. The use of process requires only that two different chelating agents, which are actually byproducts from a chemical manufacturing plant, be poured together simultaneously. The procedure can be accomplished with very simple equipment, which is easily installed. The results are environmental protection for the public, plus complete recovery of the chromium for reuse.

INTRODUCTION

Environmental concerns are in a dynamic state all over the world. During the past twenty years, we have seen a change in philosophy from near total neglect of the effects of industrial pollution to the realization, by responsible people of its serious effects. (1) The most recent philosophy, in response to the economic problems experienced worldwide, is that "pollution control is good business." In some developing countries and emerging industrial nations, pollution control is a high priority rather than just a minor concern. This was clearly expressed by Dr. Mostafa K. Tolba, Executive Director of the U.N. Environment Program at the World Industry Conference on Environmental Management. (2)

The environmental pollution problems in China, especially in Shanghai, are still in some degree of disorder. Pollutants are still being dispersed with carelessness. Recently, however, the governments of Shanghai and the People's Republic of China are beginning to handle toxic substance control programs as one of the city's main priorities. Previous regulations only limit the effluent contents as a percent of volume, but not in accordance with the quantity of pollutants.

In the past 35 years since the liberation of China, the major attention to industry was on production, and only secondarily was emphasis placed upon pollution control. Shanghai is an old-style city: All the sewer lines are outmoded and currently not available to all sites. Moreover, the old-style city construction has still not been altered and upgraded. Some factories dilute the effluent prior to pipeline discharge. Factories located at the side of the river might even discharge directly into the river. Most of the managers and directors of the factories are only concerned with production and do not care about pollution control. They would rather pay the fines involved since they consider them to be minimal and furthermore such fines are not paid out of their own pockets.

A wise man, who is deeply interested in protecting Shanghai's environment, suggested dispatching the electroplating plants and disbursing them throughout the countryside to avoid polluting the city. But he did not know that the government could best control the industry only when the pollutors are concentrated and not when they are dispersed. According to the geographical and hydrological situation in China, most of the rivers flow eastward, as illustrated in Figure 1. The Yantse

River, which passes through Shanghai, flows into the sea. Therefore, all pollutants from the countryside would be passed through Shanghai (see Figure 2).

The People's Republic of China now intends to improve environmental protection. However, most of the Chinese cadres have not yet gained acceptance of this new policy. There is a serious shortage of practical knowledge and experienced people in China concerning wastewater treatment technology and management.

The alternative idea to disbursing the electroplating plants is that of using large volumes of water to dilute the effluents to a point where they are acceptable in the discharge. This method can be employed only where water is available and the receiving river can tolerate the discharge. In an increasing number of cases, this method is not applicable. Even where it is, some treatment procedures are usually necessary, such as reduction of chromates and pH adjustment. If dilution is to be applied to meet discharge limits, it is better to do so after treatment of the more concentrated or more toxic rinse waters.

PROBLEM IDENTIFICATION

Most metal finishing operations involve two main processes. The first consists of treating the workpiece in a solution or chemical process tank, and the second consists of removing excess chemicals, that is rinse, from the workpiece (i.e., the rinse process). This excess chemical is called "drag out." Typical electroplating plant processing operations for chromium are shown in Figure 3.

Chromium is extremely toxic in its hexavalent form. Hexavalent chromium in plating rinse waters must be reduced to the trivalent form, which is much less toxic (see Figure 3, Typical Chromium Plating Line).

CONVENTIONAL METHODS FOR TREATMENT OF CHROMIUM WASTES

The treatment of rinse waters from chromium plating operations usually consists of one or a combination of the following procedures:

1. Reduction of hexavalent chromium to the trivalent form followed by the precipitation of the reduced chromium as the hydroxide.
2. Reclamation of chromic acid from the more concentrated rinse stream by evaporation or ion exchange techniques.
3. Removal of hexavalent chromium by the addition of compounds that form insoluble salts (e.g., barium chromate).

Reduction of Hexavalent Chromium and Precipitation of Chromic Hydroxide

Methods for reduction of hexavalent chromium vary with each particular plant. Common reducing agents are gaseous sulfur dioxide; sodium bisulfite, metabisulfite, or hydrosulfite; and ferrous sulfate.

Reduction with sulfur dioxide (SO_2) is the method most commonly employed by many large plating plants. Basic equipment for this method consists of sulfonators for combining sulfur dioxide with water and agitated tanks for conducting the reduction. During reduction sulfuric acid is normally added to maintain an acid solution with a pH range of 2.0 to 3.0. Under these conditions, the following reactions occur:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

(Sulfur dioxide) (Water) (Sulfurous acid)

$$2CrO_3 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + 3H_2O$$

(Chromic acid) (Sulfurous acid) (Chromic sulfate)

The approximate chemical usage is 1 gram of SO_2 per gram of chromic acid (CrO_3) in the waste solution.

PURPOSE

After a series of laboratory experiments, I have begun a pilot-scale batch trial. It is expected that the following will be achieved:

- Elimination of chromium VI and chromium III in the effluent.
- Elimination of the toxic off gases from the reaction vessels.
- Elimination of trace concentrates of chromium VI and III from the sediments and sludges.
- Utilization of a simple and easy technology.
- Simplification of installation and equipment.
- Recovery and reuse of the chromium and rinse water.

APPROACH

Currently, the prevailing treatment in China for most of the electroplating plants involves adding ferrous sulfate and sodium hydroxide to waste chromium liquor. This forms precipitates of chromium hydroxide. These are collected as dried sediments, stored in ragged bales, and left on the ground out in the open air. To my knowledge, this procedure is conducted everywhere in China.

Another available process is to use an ion exchange method, but this has two shortcomings: First, the resulting chloride ion causes harm when the wastewater is reused, and second, the price of ion exchange resin often is too high. The method that I selected and report here uses sodium ferrocyanide (NFC) together with a tertiary amine, which serve respectively as chelating and emulsing agents. However, this method is comparatively expensive.

As an alternative method, I used the black liquor from the wastewater diethylamine manufacturing plant. Excellent experimental results were achieved from both laboratory test and batch-scale operations, which gave similar results. I found that there was 0.7 mg/l chromium remaining in effluent when I used NFC alone. In the following step, I added the black liquor containing the diethylamine. The results indicated there was no trace of chromium within the effluent or the resulting sediments. The amines have the capacity for reacting with hexavalent chromium in acidic solutions by the following mechanism.

$$2R_3N \quad + \quad Cr_2O_7^{=} + 2H^{+} \rightarrow (R_3NH)_2\,Cr_2O_7$$

(amine)	(dichromate ion in acidic chrome rinse waters)	(compound of amine with dichromate with negligible solubility in water)

The following table expresses the results achieved by the reaction of chelating agents on NFC using various metal ions other than chromium.

Metal Ions	Precipitate Color	Adsorption/ Dissociation	Solute
Na^{+}	N/A		sl
K^{+}	N/A		sl
Fe^{++}	Blue		
Fe^{+++}	Dark Blue		
Uo^{++}	Brown		
Mn^{+}	Light Green		
Co	Bluish Green		
Cu	Red		
Zn	White		

Metal Ions	Precipitate Color	Adsorption/ Dissociation	Solute
Pb	Yellowish White		
Sn		Disso.	
Sr			sl
Al			sl
Cd	White		
Au			s
Ag	White		
Ca			s
Ba			s
U	Brown		
Th	White		
Cs		Adsorb	
Mg		Adsorb	
Mo		Adsorb	
V			s
Tl			sl
Ga			s

Character

Cyanide (CN) is tightly bonded with iron in ferrocyanide form and therefore is not easily decomposed. This reaction takes place at room temperature and in a diluted acidic solution. Finally, the sodium ferrocyanide can be recycled and reutilized, but tertiaryamine is decomposed. This process is quite safe and inexpensive. NFC can be chelated in the presence of many metal ions. It appears that neither a precipitation nor turbide solution form during the reaction. Meanwhile, NFC chelated with nickel is green in color. Chelated with copper it is red; with zinc, white; and with lead, a light yellowish white. When it is chelated with chromium, no color develops.

The following shows the affinity of metal ions with Oxygen (O) and Nitrogen (N). (The relation is arranged in series.)

O > N Mg, Ca, Sr, Ba, In, Tl, Ti, Zr, Th, Si, Ga, Sn, V^{+5}

V^{+4}, Cb, Te, Mo, U^{+6}, U^{+4}, Fe^{+3}, Co^{+2}

N > O Cu^{+}, Ag^{+}, Au, Cu^{+2}, Cd, Hg, V^{+3}, Co^{+3}, Ni^{+2}

All above relations of affinity never mention chromium. It was learned that the radius of the chromium ion is 0.3A.

Chemical Reaction

$Cr_2(SO_4)$ and $Na_4Fe(CN_6)$ no evidence

$Cr_2(SO_4)^3$ and $R_4Nx\ Cr(NHR_3)H_2O$

where n = 1 - 5

R = $C^1 - C^8$

When the effluent contained Nickel (Ni), Copper (Cu), and Iron (Fe), it reacted with ferrocyanide, producing various colored precipitates shown in the table above.

THE RESULTS

By means of the described co-treated method of NFC and black liquor wastewater, the final test of the effluent and sludges resulted in satisfactory concentrations.

Test No.	Cr (mg/l)	
	6+	3+
1	0.05	0.45
2	0.01	0.09
6	0.07	
7	nil	nil
8	nil	nil

Tests 1 and 2 use NFC alone.
Test 6 is the test of effluent in the batch trial.
Tests 7 and 8 are the sludge analysis when NFC is used with black liquor.

The results of the laboratory and field batch trials confirm that NFC and wastewater black liquor from a diethylamine manufacturing plant can be used to effectively and inexpensively treat toxic chromium from metal finishing plants.

ACKNOWLEDGMENTS

The analytical laboratory support service was received from the Sanitation and Epidemic Prevention Station of QIN-AN District of Shanghai. The reuse of the chromium sludge was sponsored by Mr. Zee Yi-din. He is the Assistant Engineer in the Dah-fong Chemical Factory of Shanghai, Peoples Republic of China.

REFERENCES

1. George Rey, William J. Lacy, and Allen Cywin, "Industrial Water Reuse: Future Pollution Solution," Environmental Science and Technology, Vol. 5, No. 9 (1971).

2. Mostafa, K. Tolba, "World Industry Conference on Environmental Management," United Nations Environmental Programme, Versailles, France, November (1984).

3. F. P. Dwyer and D. P. Mellor, "Chelating Agents and Metal Chelates."

4. E. Arthur Martell and Melvin Calvin, "Chemistry of the Metal Chelate Compound."

5. An Anorg. Allgn. Chemia (321) 175-9.

6. Ibid., 180-3 (1963).

7. International Solvent Extraction Conference (1980).

8. University Rajptana Studies Physical Science (1962) 45-55.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

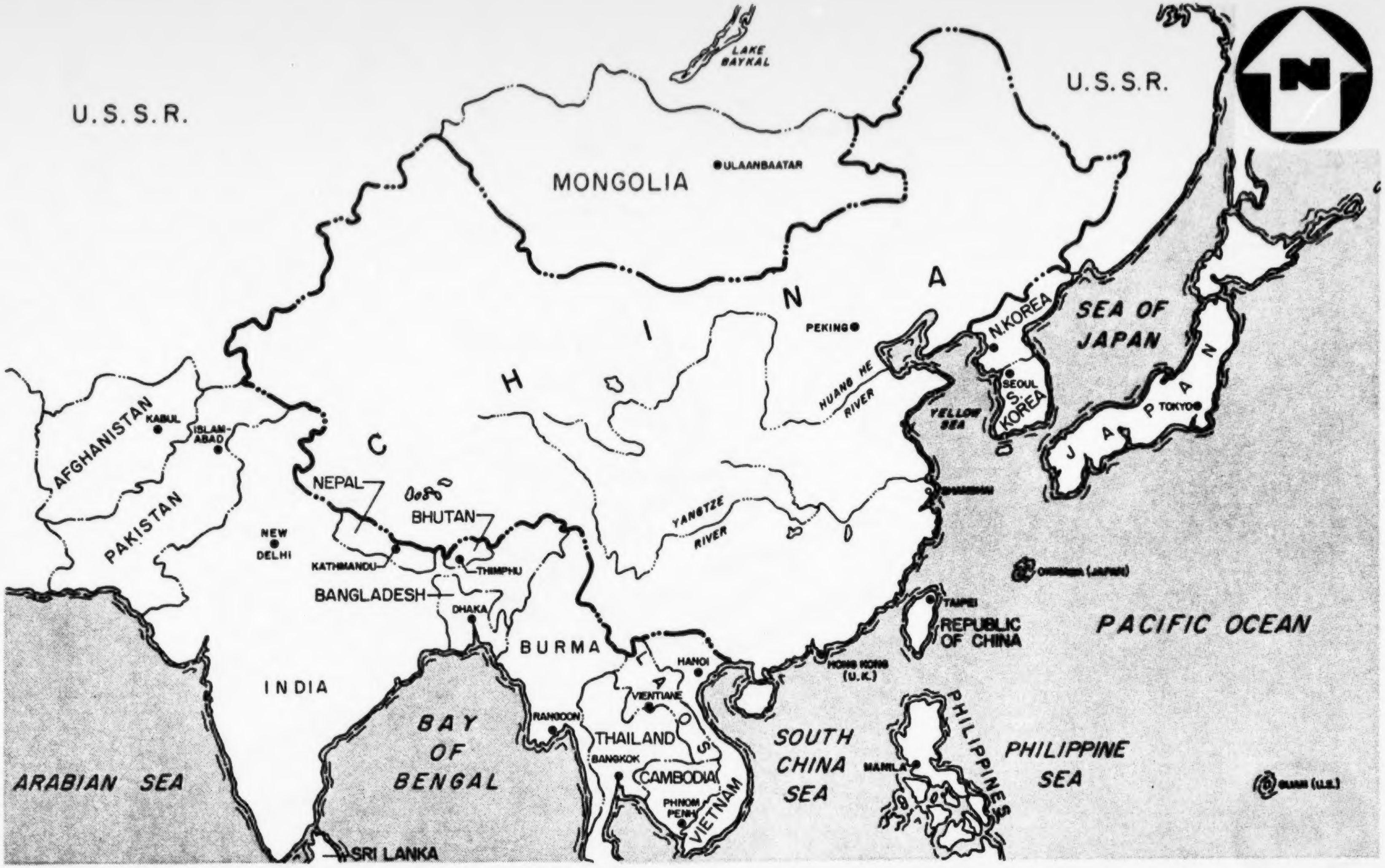

U.S.S.R.
LAKE BAYKAL
U.S.S.R.
MONGOLIA
ULAANBAATAR
C H I N A
PEKING
HUANG HE RIVER
YANGTZE RIVER
AFGHANISTAN
KABUL
ISLAMABAD
PAKISTAN
NEW DELHI
NEPAL
BHUTAN
KATHMANDU
THIMPHU
BANGLADESH
DHAKA
INDIA
BURMA
RANGOON
LAOS
VIENTIANE
HANOI
THAILAND
BANGKOK
CAMBODIA
PHNOM PENH
VIETNAM
N.KOREA
S.KOREA
SEOUL
YELLOW SEA
SEA OF JAPAN
JAPAN
TOKYO
SHANGHAI
OKINAWA (JAPAN)
TAIPEI
REPUBLIC OF CHINA
HONG KONG (U.K.)
PACIFIC OCEAN
PHILIPPINES
MANILA
PHILIPPINE SEA
GUAM (U.S.)
SOUTH CHINA SEA
BAY OF BENGAL
ARABIAN SEA
SRI LANKA
N

FIGURE 1 - CHINA AND VICINITY

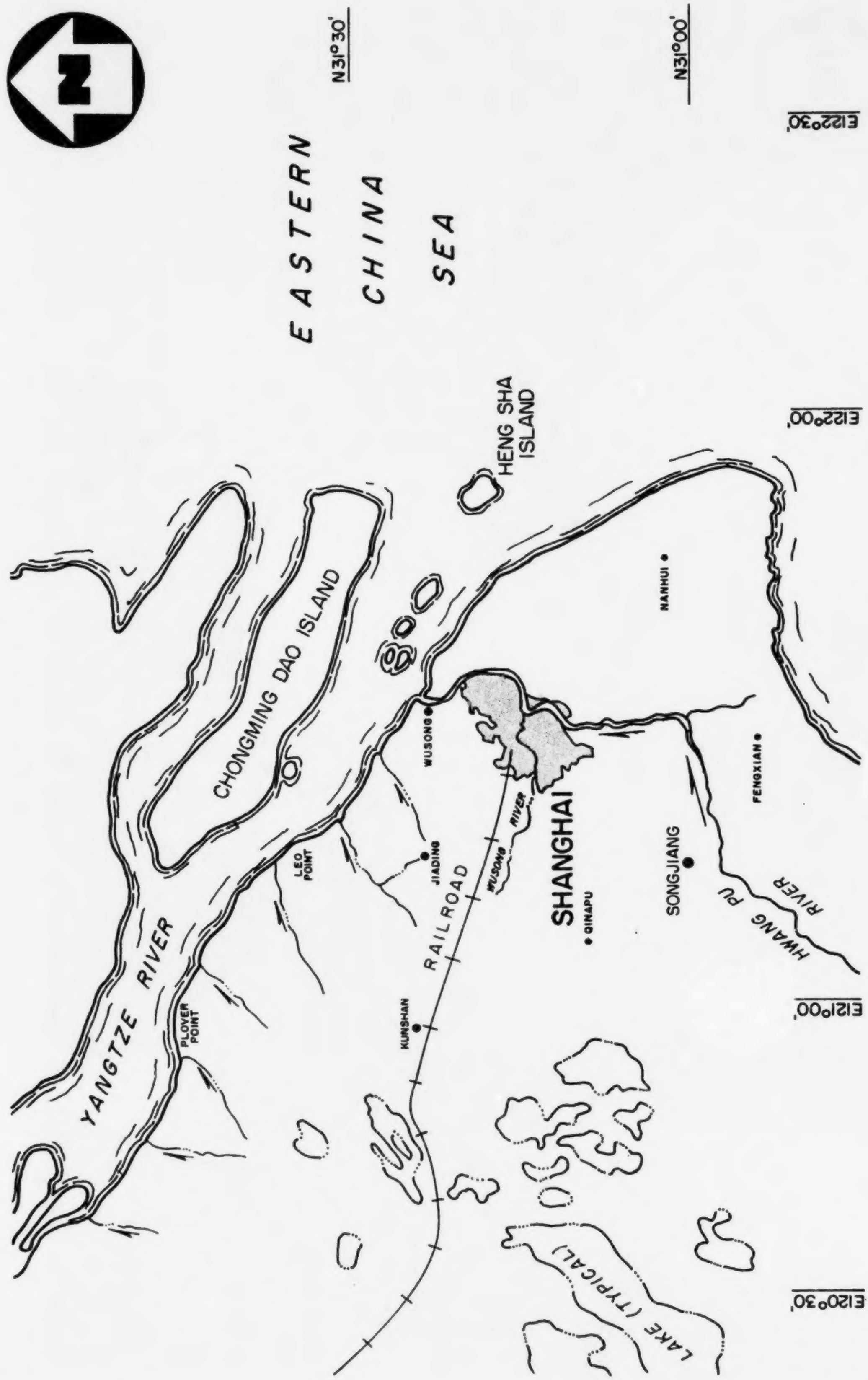
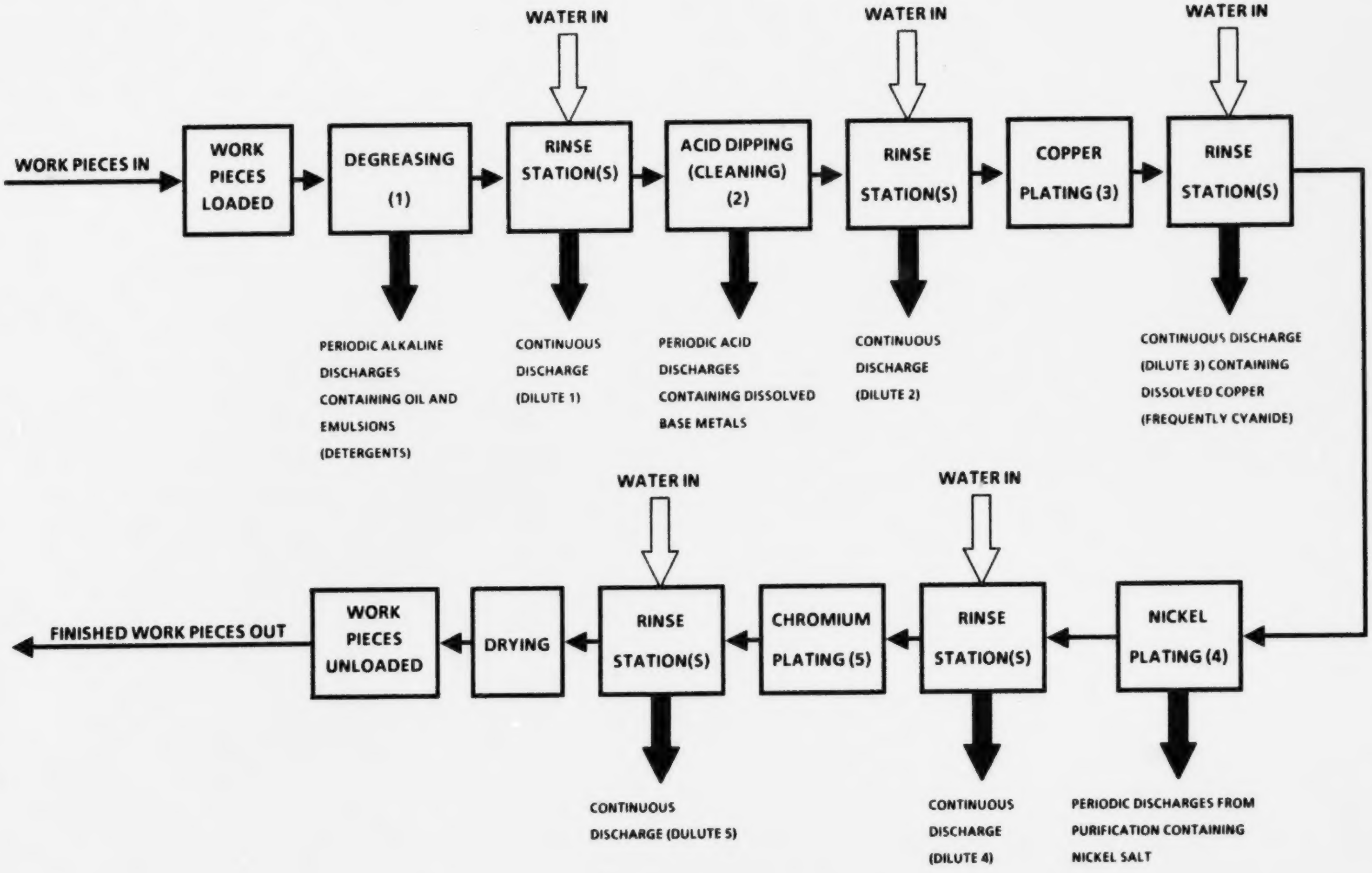

N
N31°30'
N31°00'
E122°30'
E122°00'
E121°00'
E120°30'
EASTERN
CHINA
SEA
HENG SHA ISLAND
CHONGMING DAO ISLAND
YANGTZE RIVER
PLOVER POINT
LEO POINT
WUSONG
JIADING
KUNSHAN
RAILROAD
WUSONG RIVER
SHANGHAI
QINAPU
SONGJIANG
FENGXIAN
NANHUI
HWANG PU RIVER
LAKE (TYPICAL)

FIGURE 2 - SHANGHAI AND VICINITY

FIGURE 3

TYPICAL CHROMIUM PLATING LINE


WORK PIECES IN
WORK PIECES LOADED
DEGREASING (1)
WATER IN
RINSE STATION(S)
ACID DIPPING (CLEANING) (2)
WATER IN
RINSE STATION(S)
COPPER PLATING (3)
WATER IN
RINSE STATION(S)
PERIODIC ALKALINE DISCHARGES CONTAINING OIL AND EMULSIONS (DETERGENTS)
CONTINUOUS DISCHARGE (DILUTE 1)
PERIODIC ACID DISCHARGES CONTAINING DISSOLVED BASE METALS
CONTINUOUS DISCHARGE (DILUTE 2)
CONTINUOUS DISCHARGE (DILUTE 3) CONTAINING DISSOLVED COPPER (FREQUENTLY CYANIDE)
NICKEL PLATING (4)
WATER IN
RINSE STATION(S)
CHROMIUM PLATING (5)
WATER IN
RINSE STATION(S)
DRYING
WORK PIECES UNLOADED
FINISHED WORK PIECES OUT
PERIODIC DISCHARGES FROM PURIFICATION CONTAINING NICKEL SALT
CONTINUOUS DISCHARGE (DILUTE 4)
CONTINUOUS DISCHARGE (DULUTE 5)

REUSE OF WASTE FERROUS SULPHATE

Lucjan PAWŁOWSKI nad Marek KOTOWSKI
Department of Waster and Wastewater Technology
Technical University of Lublin
40, Nadbystrzycka Str., 20-618 Lublin,POLAND

ABSTRACT

Processes of manufacturing of the yellow, red and black iron pigments from a waste ferrous sulphate are discussed in this paper.

INTRODUCTION

Large quantity of waste ferrous sulphate generated during either production of titanium white (tittianium dioxide) or metal pickling operations creates an environmental problem with its storage. Stored in dumps, it penetrates to ground waters. In Poland, there are a few million tons of waste ferrous sulphate stored in dumps. Ferrous sulphate may be a product for:

- agriculture for production of herbicide and insecticide,
- wood preservation,
- dyeing and tanning industry,
- production of photographical developers,
- ink production,
- production of sorbents to desulphurization of natural and converter gases,
- waters and wastewaters treatment (as reductor and coagulant).

All the above applications do not utilize the huge quantities of waste ferrous sulphate and therefore the studies on new applications is of significant practical importance.

Production of iron pigments from waste ferrous sulphate seems to be a proper way of its utilization. The demand for these pigments in Poland is about 40000 tons per year and it is almost all imported. According to literature, the greatest application and demand have been obserbed for yellow (α - FeOOH), red (α -Fe_2O_3) and black iron pigments (Fe_3O_4- magnetite). Among the iron pigments, the yellow one is commercially most important because it is widely used for production of dyes, magnetic supports and for manufacturing red and black pigments.

AIM OF STUDY

The aim of the study is to work out a simple method of manufacturing the yellow iron oxide pigment from waste ferrous sulphate generated as a waste product during production of titanium white.

The manufacturing of yellow iron oxide pigment may be carried out by:

- oxidation of solution of Fe(II)

Preceding page blank

salts in the presence of metalic iron in acidic environment |Matsuo Y.;1954; Oda M.;1960a|;

- oxidation of suspension of $Fe(OH)_2$.

Such oxidising agents as chlorates |Edwards W.H.;1962|, hypochlorites |Krause A.;1955a|, nitrobenzene |Riskin J.;1946|, H_2O_2 |Krause A.; 1955a; Krause A.;1963b|, oxygen |Voigt C.W.;1948| and air |Kashereninov G.O.;1968| are most frequently used. For neutralization one of the following agents: NaOH |Oda K.;1969b; Northern Pigment Co. Ltd 1964|, Na_2CO_3 |Riskin J.;1946|, $Fe(OH)_2$ |Minot M.A.;1949|, gaseous NH_3 or its aqueous solution |Naganuma U.;1963a; Naganuma U.; 1968b|, may be used.
The oxidation reactions can be depicted by eqs.:

$$4Fe^{+2} + O_2 + 8OH^- - 4FeOOH + 2H_2O$$

$$4Fe(OH)_2 + O_2 \quad - 4FeOOH + 2H_2O$$

$$4Fe^{+2} + O_2 + 4H_2O - 4FeOOH + 4H^+$$

When NaOH is used for neutralization, waste solution left after separation of α - FeOOH contains Na_2SO_4 and NaOH, what makes such wastewater treatment more complicated.In the case when NH_3 is used for neutralization, the waste solution contains only $(NH_4)_2SO_4$. Utlilization of such wastewater is easier.

Therefore, we have decided to study only these processes where NH_3 is used for neutralization, using two procedures:

- precipitation of Fe(II) in the form of $Fe(OH)_2$ with stoichiometric amount of NH_3 and aeration of slurry with air for oxidation of Fe(II) to Fe(III);
- fractional precipitation of Fe(II) in the form of $Fe(OH)_2$ with NH_3 and aeration of each fraction (together with whole solution) with air for oxidation Fe(II) to Fe(III).

There were two series of experiments. First one, when solution of $FeSO_4$ was prepared by dissolution of a ferrous sulphate in pure water and the second one, when the ferrous sulphate was dissolved in solution of $(NH_4)_2SO_4$.

RESULTS

As Figs 1 and 2 show, it is imposible to obtain iron oxides pigments when, before aeration, the total amount of Fe(II) is precipitated in one step with a stoichiometric amount of ammonia. Depending on a concenzration of the ferrous sulphate in a solution (see Fig.1) and intensity of aeration (see Fig.2), the following products of oxidation of Fe(II) to Fe(III) were obtained. That is:

- pure $Fe(OH)_3$ or one of the following mixtures;
- γ - FeOOH + $Fe(OH)_3$ + Fe_3O_4 or
- γ - FeOOH + Fe_3O_4.

Iron oxides having pigment properties were formed when a fractional precipitation and aeration of each precipitated fraction was applied. At lower intensity of aeration i.e. 10 to 15 m^3/hm^3 the yellow pigment (α -FeOOH) was formed, while at intensity of aeration 50 m^3/hm^3 the orange pigment (γ -FeOOH) was formed, and at intensity of aeration between these values amixture of α - FeOOH and γ -FeOOH was obtained, which have colour changing from yellow via yellow-orange to orange.

Mechanisms of the oxidation reaction Fe(II) to Fe(III) were not thououghly studied, however some qualitative observations were made. It was found, that there are three stages of the oxidation reactions (see Fig.3):

- the 1st etage, where the reactions produce an excess of hydrogen ions

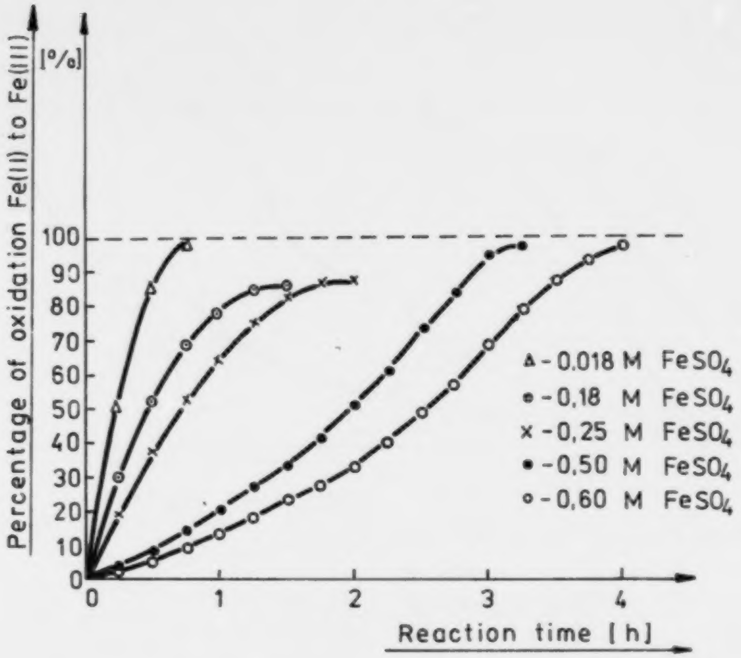


Fig. 1. Procentage of oxidation Fe(II) to Fe(III) as a function of reaction time for various concentrations of the ferrous sulphate. Intensity of aeration 120 m^3 of air/hm^3 of solution. Final products: △ - $Fe(OH)_3$; ⊙ - Fe_3O_4 + γ - FeOOH + $Fe(OH)_3$; × - Fe_3O_4 + γ - FeOOH; ● - Fe_3O_4 + γ - FeOOH; ○ - Fe_3O_4 + γ - FeOOH; - $Fe(OH)_3$ + + - FeOOH.

and therefore ph drops from 8 to 6;

- the 2 nd stage where pH is stable around value of 6. In this stage so called "rust green II" $|4Fe(OH)_2 . 2Fe(OH)_3 . FeSO_4 . nH_2O|$ is formed;
- the 3rd stage, where again the reactions produce an excess of hydrogen ions and therefore pH drops from 6 to 3.

The stages are observed during aeration of each of four fractions.

A flowsheet of the process based on fractional precipitation and oxidation is depicted in Fig.4. In a reactor, a solution of the ferrous sulphate was mixed with 25% of stoichiometric amount of ammonia, then aerated till the sludge in the reactor reached yellow colour. Then the next portion of 25% ammonia was added and a mixture was aerated untill the sludge reached again yellow colour. This operation was repeated four times.

In the next operation a sludge was separated from a solution of the ammonium sulphate. The sludge was rinsed with water circulating via a strongly basic anion exchanger which was regenerated with a 4% solution of the sodium hydroxide. A regeneration effluent containing the sodium sulphate is discharged as a wastewater.

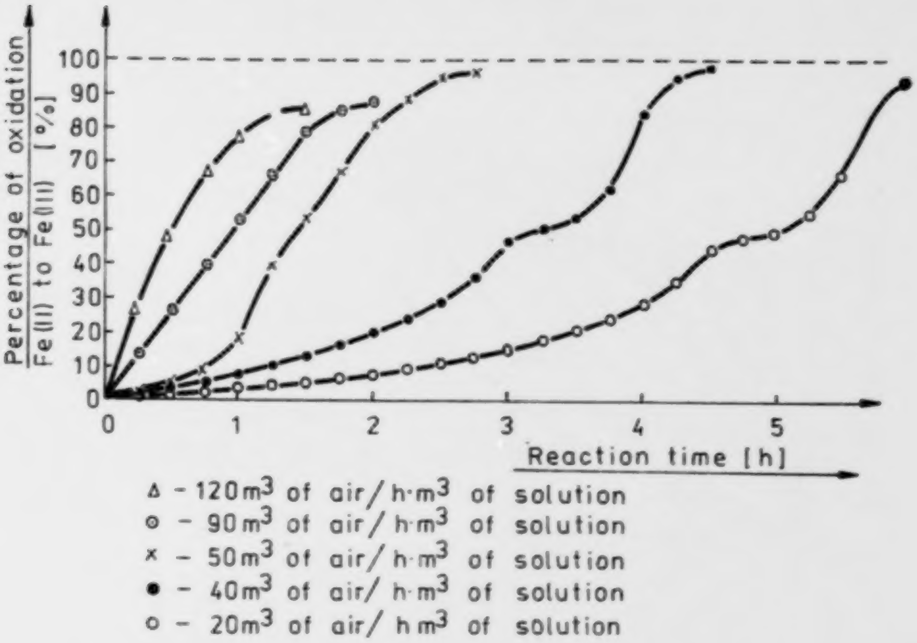


Fig. 2. Procentage of oxidation of Fe(II) to Fe(III) in 0.18 M solution of the ferrous sulphate as a function of time for various intensities of aeration. Final products: △ - $Fe(OH)_3$ + Fe_3O_4 + γ - FeOOH; ⊙ - $Fe(OH)_3$ + Fe_3O_4 + γ - FeOOH; × - Fe_3O_4 + γ - FeOOH; ● - Fe_3O_4 + + γ - FeOOH; ○ - Fe_3O_4 + γ - FeOOH.

The rinsed sludge was directed onto a spry-dryer where the powdered yellow iron oxide pigment was formed.

The solution containing $(NH_4)_2SO_4$ from filtration was directed to an ammonia stripper, alkalized with CaO and ammonia was stripped by mixture of vapour form the spray-dryer and air.

The stripped ammonia was used for precipitation of the ferrous hydroxide. Waste solid calcium sulphate and wastewater containing about 2 g $CaSO_4/dm^3$ are formed, during stripping of the ammonia.

It was found that when the aerated mixture of the ferrous hydroxide and sulphate contains at least 0.018 M of the ammonium sulphate, the yellow iron oxide pigment (- FeOOH) obtained has brighter colour due to finer dispersion. In this process a part of the ammonia sulphate obtained during filtration of the pigment was recycled for preparation of a solution of the ferrous sulphate. This process has two advantages i.e.: it allows to obtain better pigment and, the wastewater (solution of the ammonium sulphate) of higher concentration, and one disadvantage i.e. slower rate of oxidation Fe(II) to Fe(III),

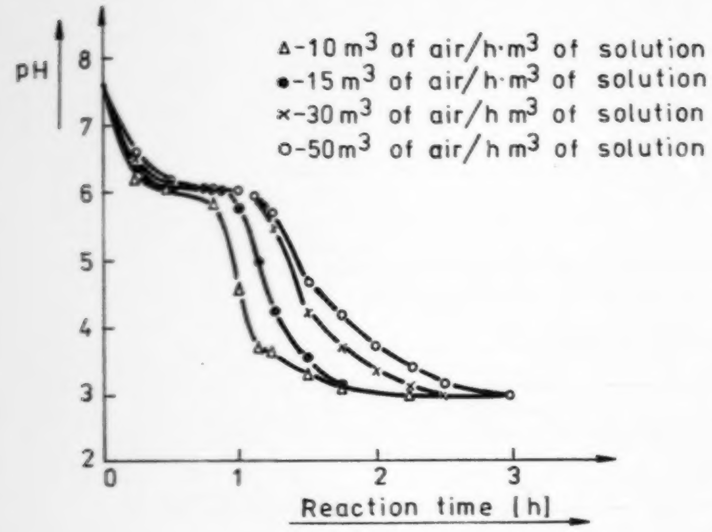


Fig. 3. Influence of reaction time on pH of the aerated solution of the 0.5M ferrous sulphate. Before aeration 25% of Fe(II) was precipitated in a form of $Fe(OH)_2$ with ammonia. Final products: Δ - α - FeOOH; ● - α - FeOOH; × - α - FeOOH + γ - FeOOH; o - γ - FeOOH.

which decreases with an increase of a concentration of the ammonium sulphate in a solution of the ferrous sulphate to be oxidized (see Fig. 5 and 6).

The ferrous sulphate may be used also for manufacturing of red and black pigments (see Fig. 7). The red pigment was obtained by calsination of the yellow pigment. To obtain the black pigment (see right side of Fig. 7) it was necessary to heat a solution containing a mixture of the ferrous sulphate and hydrogen piroxide (H_2O_2) to temperature 80-95°C, and then to add a stoichiometric amount of ammonia during stirring. The black pigment obtained was then separated, rinsed and dryed on spray-dryer.

A solution of the ammonium sulphate leaving a filtration unit was directed to an ammonia stripping unit. The ammonia recovered, in the stripper was used for fractional precipitation of the ferrous hydroxide.

The processes depicted in Figs. 4 and 7 allow to "convert" an usless waste ferrous sulphate into the useful iron oxide pigments. Disadvantage of these processes is that although the waste ferrous sulphate is elimnated, a problem of a protection of the environment still exists, because new wastes, solid calcium sulphate and wastewaters containing calcium and sodium sulphates are generated. Fortunately, they are less harmful. However, it is possible to eliminate the waste calcium sulphate and its solution by utilization of the ammonium sulphate as a fertilizer. Usually, the solution will need to be concentrated or

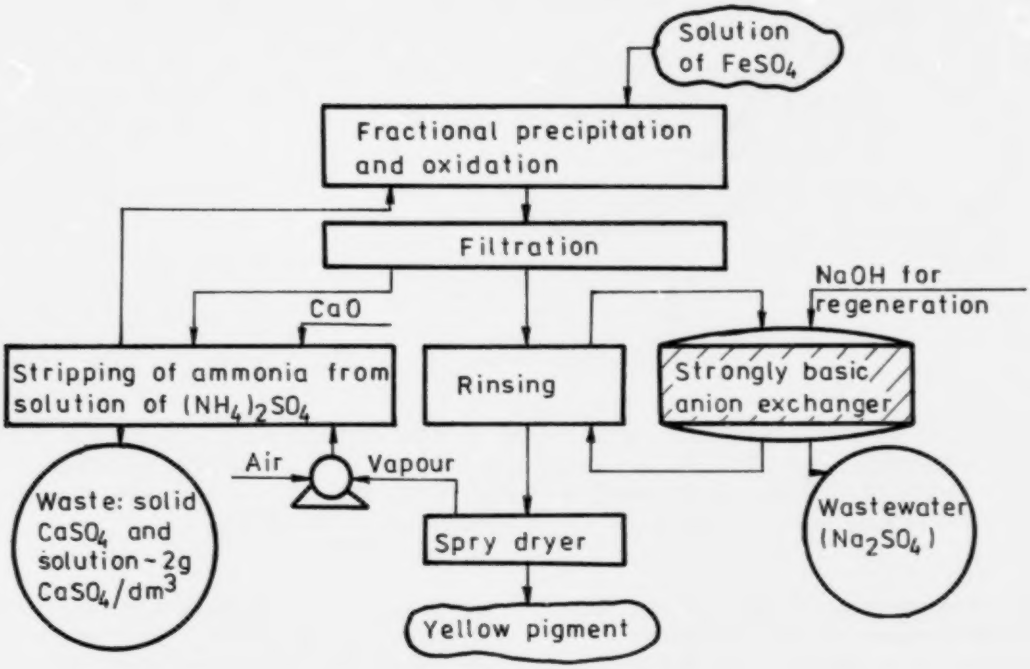

Solution of $FeSO_4$
Fractional precipitation and oxidation
Filtration
CaO
NaOH for regeneration
Stripping of ammonia from solution of $(NH_4)_2SO_4$
Rinsing
Strongly basic anion exchanger
Air
Vapour
Waste: solid $CaSO_4$ and solution ~ 2g $CaSO_4/dm^3$
Spry dryer
Wastewater (Na_2SO_4)
Yellow pigment

Fig. 4. A flowsheet of the process for production of the yellow iron oxide pigment from the waste ferrous sulphate.

even solidified by evaporation.

ACKNOWLEDGMENT

We gratefully acknowledge the financial suport of the CPBP No 03.08. we also acknowledge the expert technical assistance of Mrs. Grażyna Młodawska, Miss Ewa Smulkowska and Mrs. Elżbieta Żołnierczuk.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

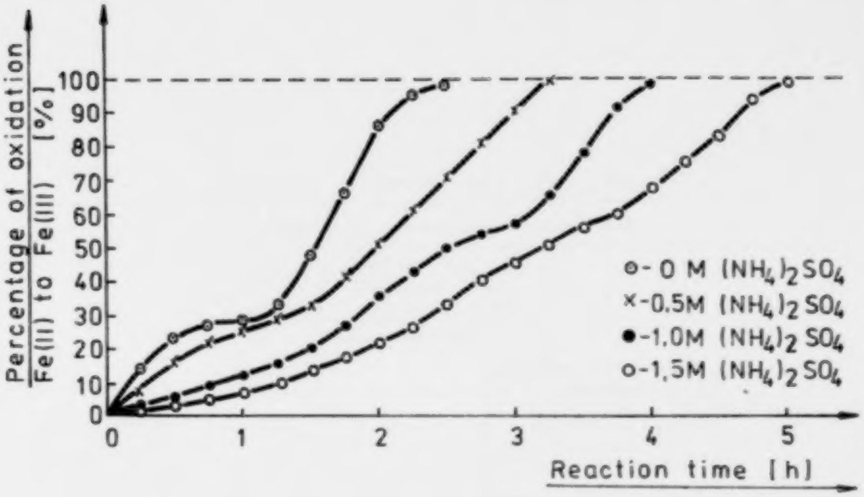


Fig. 5. Procentage of oxidation of Fe(II) to Fe(III) as a function of reaction time for various concentration of the ammonium sulphate in a mixture with 0.5M solution of the ferrous sulphate. Intensity of aeration 10 m^3 of air/hm^3 of solution. Final products: ⊙, ×, ●, ○, - α - FeOOH.

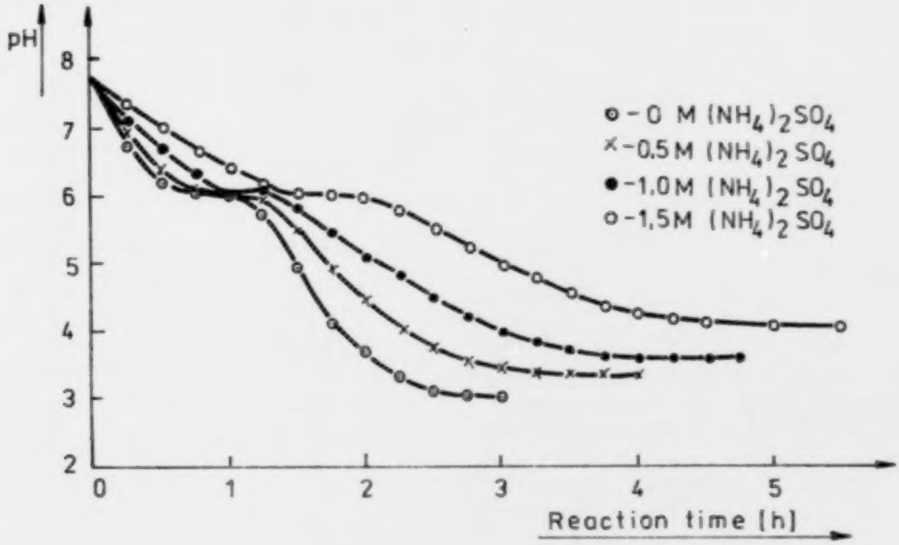


Fig. 6. Influence of reaction time on pH of the aerated for various concentration of the ammonium sulphate in a mixture with 0.5M ferrous sulphate. Before aeration 25% of Fe(II) was precipitated in a form of $Fe(OH)_2$ using ammonia. Intensity of aeration 10 m^3 of air/hm^3 of solution. Final products: ⊙, ×, ●, ○, - α - FeOOH.

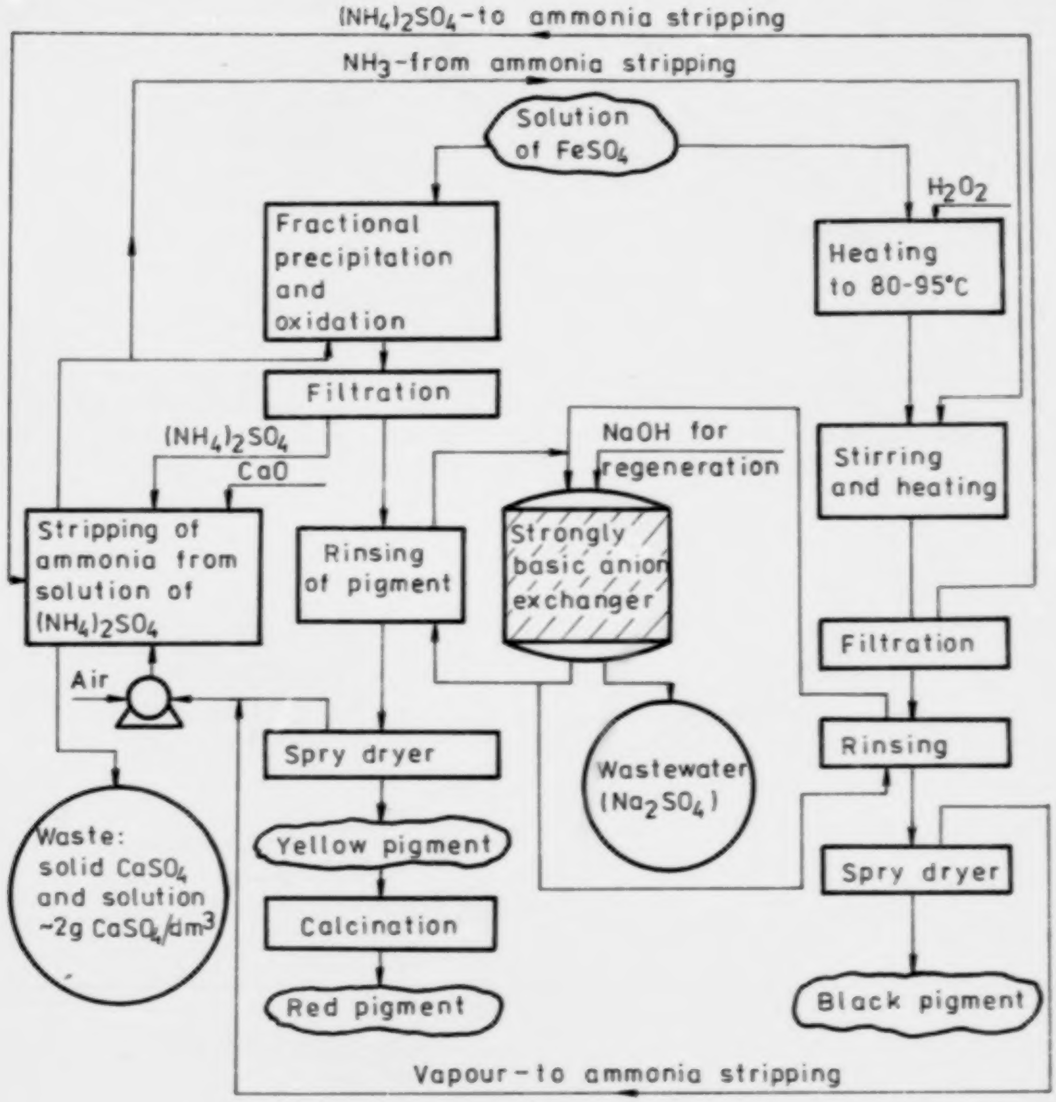

$(NH_4)_2SO_4$-to ammonia stripping
NH_3-from ammonia stripping
Solution of $FeSO_4$
Fractional precipitation and oxidation
H_2O_2
Heating to 80-95°C
Filtration
$(NH_4)_2SO_4$
CaO
NaOH for regeneration
Stirring and heating
Stripping of ammonia from solution of $(NH_4)_2SO_4$
Rinsing of pigment
Strongly basic anion exchanger
Filtration
Air
Spry dryer
Rinsing
Wastewater (Na_2SO_4)
Waste: solid $CaSO_4$ and solution ~2g $CaSO_4$/dm^3
Yellow pigment
Spry dryer
Calcination
Red pigment
Black pigment
Vapour-to ammonia stripping

Fig. 7. A flowsheet of the process for production of yellow, red and black iron oxides pigments from the waste ferrous sulphate.

REFERENCES

1. Edwards, Webster H.; U.S. Pat. 3,052,644; 4 September 1962;

2. Kasherininov G.O.; USSR Pat. 213 996; 20 March 1968;

3. Krause A., Krang M., Fijałkowska J.; Chem. Abstr. 55(1961), 17333;

4. Krause A., Zieliński S.; Chem. Abstr. 59 (1963), 7753

5. Matsuo Y, Tanaka H.; Jap. Pat. 8018/54; 7 December 1954;

6. Minot, M.A.; Fr. Pat. 953-329; 5 December 1949;

7. Naganuma U.; Jap. Pat. 17652/ /63; 10 September 1963;

8. Naganuma U.; Jap. Pat. 11661/68; 16 May 1968;

9. Northern Pigment Co. Ltd.; Can. Pat. 698.715; 24 November 1964;

10. Oda K.; Jap. Pat. 28,372/69; 21 November 1969;

11. Oda M.; Kagitani T.; Jap. Pat. 9027/60; 12 July 1960;

12. Riskin J., Velikoslavinskaya T.; J.appl. Chem. (USSR), 19 (1946), 262;

13. Voigt, C.W.; Chem. Abstr.; 42 (1948) 70 62 e.

Disclaimer

The work in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

BARIUM RECOVERY FROM SPENT HARDENING SALTS

Ryszard Szpadt and Marta Sebastian
Institute of Environment Protection Engineering
Technical University of Wrocław
PL 50-370 Wrocław,Poland

ABSTRACT

Spent hardening salts contain water-soluble barium chloride and are, therefore, classified as waste substances creating serious environmental hazards. Since those hazardous wastes are produced in relatively small amounts by a number of plants working for the metal industry of Poland, they have usually been disposed of at municipal or industrial dumping sites which are not suitable for receiving such loads. In this paper the composition and physico-chemical properties of spent salts, water extracts and extraction residues are characterized. Attempts have also been made to recover barium from water extracts by precipitation of low-solubility salts, barium sulphate and barium carbonate. Owing to a high degree of purity, recovered salts are suitable for reuse.

Technological systems enabling barium salts recovery and disposal of extraction residues are suggested. Keeping in mind that the wastes of interest are produced in a number of sources scattered throughout the country, barium salts recovery should be carried out only on a nation-wide or at least on a macroregional scale. The most recommendable concept is that involving treatment and regeneration by the manufacturer. The waste management concept proposed has two inherent advantages - it enables barium recovery and reuse, thus abating environmental pollution from this specific hazardous waste.

INTRODUCTION AND PURPOSE

The most common hardening method to be encountered in the machine-building industry of Poland is the application of salts containing barium chloride as a main component. Displaying a high water-solubility, barium chloride can easily penetrate the environment, and particularly ground-

and surface waters, thus creating serious hazards to municipal water supply systems. These hazards will manifest especially when spent salts are disposed of inappropriately, e.g. by storage on municipal or industrial dumping grounds which fail to meet the sanitary standards required. And this is a frequent practice in the metal industry of Poland. Implementing an adequate system for the collection and processing of such wastes should help not only in the abatement of environmental contamination by a toxic substance, but also in the reasonable recovery or reuse of barium salts (1,2,3).

Spent and contaminated salt baths produce two major kinds of wastes:

(a) spent hardening salts, routinely removed from the salt furnace, and

(b) impurities (removed regularly, at least once a week, from the furnace bottom) consisting of small iron fillings, ash, dust particulates, melted salts and salt degradation products.

There is only a slight difference in the composition between the two types of wastes - spent hardening salts contain less impurities than do the wastes removed from the salt furnace bottom. In this paper consideration is given to the type itemized as (b), because these wastes are more difficult to treat.

The objective of the study (4) was to determine the composition and physico-chemical properties of the wastes, water extracts and extraction residues, to develop methods of barium recovery from water extracts in carbonate or sulphate form, and to present a general concept of waste barium salt management in Poland.

APPROACH

The experiments were run on a laboratory scale and involved 17 samples, which had been milled to obtain grain size <2 mm.

Physico-chemical analyses and technological investigations included the following:

- determination of Ba, Sr, Fe,Na,K,Ca,Mg,Pb,Zn,Ni,Cu,Cr, Cd,Mn and Co content in salt wastes by atomic absorption in solutions after mineralization in a mixture of concentrated $HClO_4+HNO_3$ acids, using a Carl Zeiss-Jena AAS1 spectrophotometer.
- thermogravimetry involving an OD-102 Paulik-Erdey derivatograph made by MOM Budapest.
- single- and multi-stage water extraction in order to dissolve and wash out barium chloride from salt wastes. Single-stage extraction involved mixing of 50g of waste and 1 dm^3(liter) of distilled water. After 24 h the extract was decanted. In multi-stage extraction 50g of waste were mixed with 1 dm^3 of distilled water. The extract was decanted after 4 h. The residue was subject to five extraction processes (each of them involving 250 cm^3 of distilled water) with the aim to determine barium content in successive extracts.
- determination of the composition and properties of water extracts by making use of standard methods (for water and wastewater).
- determination of the

chemical composition of the residue from extraction. Analytical procedures were the same as those for wastes.

- microscopic examinations of salt wastes and residues from extraction, using a Cambridge-Stereoscan 180 scanning microscope with a Link-System.
- precipitation of barium sulphate (using sulphuric acid or sodium sulphate solution) and barium carbonate (using sodium carbonate solution) from water extracts of salt wastes.
- approximate spectral analyse of barium sulphate and barium carbonate, using a Carl Zeiss-Jena PGS-type spectrophotometer.
- X-ray analyse of barium carbonate, making use of a Carl Zeiss-Jena TUR M-62 apparatus (radiation $Cu_{K\alpha}$) .
- thermogravimetry of barium carbonate with the use of a Q-150 OD Paulik-Erdey derivatograph made by MOM Budapest.
- purity determinations for barium sulphate and barium carbonate according to the following standards: PN-59/C-80250, ZN-54/M and PCh/05-228.

PROBLEMS ENCOUNTERED

Barium concentrations in salt wastes, water extracts and extraction residues were determined by gravimetry and atomic absorption. The gravimetric method, in which barium is precipitated by sulphuric acid, was found to be recommendable for water extracts only. Determination of barium by the gravimetric method in solution after mineralization of salt wastes or in the residue from extraction is characterized by a considerable error which should be attributed to the co-precipitation of other compounds present in the solution. Furthermore, approximate spectral analyses have shown that the barium sulphate precipitate contains Sr,Al,Fe,Na,Ca,Si,Zn, Pb,Mg,Mn and Cr in amounts grather than 10^{-2} dry wt.%.

Thus, it is the atomic absorption method that should be recommended when mineralized salt wastes or extraction residues are involved.

RESULTS

Table 1 gives the chemical composition of two SH-960 salt waste samples. As shown by these data, barium and iron occur at the highest concentrations.

Table 1. Chemical composition of two salt waste samples (dry wt. %)

Metal	Sample 1	Sample 2
Ba	34.86	36.69
Fe	30.55	21.49
Cr	1.98	0.06
Mn	0.18	0.16
Sr	0.12	0.14
Na	0.36	0.58
K	0.51	0.49
Ca	0.73	0.72

Mg,Pb,Zn,Ni,Cu,Cd and Co have not been included, because they are found in amounts below 0.04 dry wt. %.

Barium content in salt wastes accounts for 64.6 to 68.0 % of its content in fresh hardening salts.

Comparison of results for single-stage extraction and multi-stage extraction shows a distinctly higher effectiveness of the latter. It has been found that three stages are sufficient to yield satisfactory effects. But it is only the first extract that contains appropriate barium concentrations to enable recovery of barium carbonate or barium sulphate. The second and third extract should be concentrated. And this may be achieved by reusing them for the first extraction of a successive portion of wastes. In the case of Sample 1, the residue from single-stage extraction amounted to 44.28 dry wt.% of the initial value and displayed barium concentration accounting for 8 % of the initial content. The data obtained for the residues from multi-stage extraction were 39.93 dry wt.% and 4.10 % respectively. Non-extracted barium persisted exclusively in the form of low water-soluble carbonate and oxide, which was also confirmed by microscopic examinations and X-ray analyses.

Figures 1 through 9 give micrographs and maps showing the surface distribution of some elements on waste particles and in residues from single- and multi-stage extraction. They reveal a noticeable abatement of barium content and an increasing contribution of iron to the residues from multi-stage extraction (as compared to the remaining two samples) .

Technological investigations on the precipitation of barium sulphate from water extracts have shown that it is necessary to use reacting substances in slight excess (2-4 %) as compared to stoi-

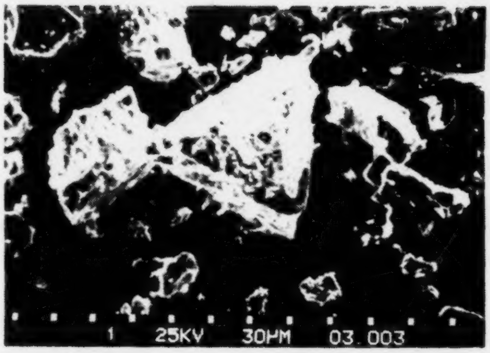


Figure 1. Backscattered electrons image of SH-960 salt waste.

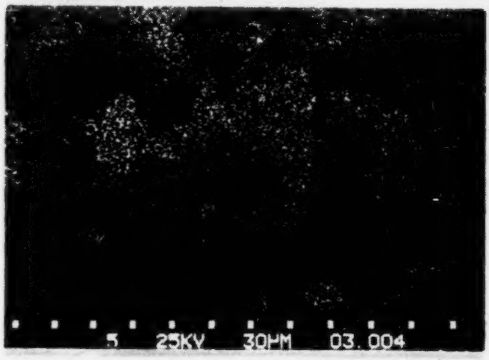


Figure 2. Distribution of $\mathrm{Ba}_{k\alpha}$ in the region of Fig. 1.

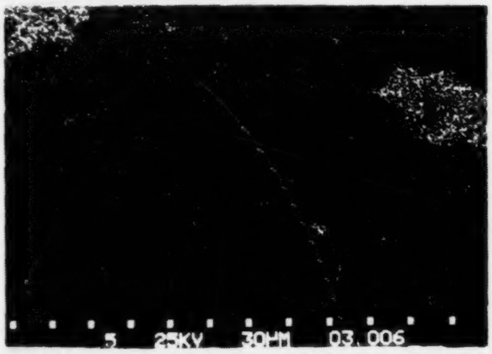


Figure 3. Distribution of $\mathrm{Fe}_{k\alpha}$ in the region of Fig. 1 .

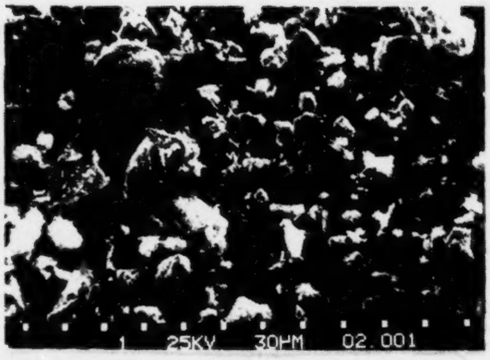

1 25KV 30µM 02.001

Figure 4. Backscattered electrons image of SH-960 salt waste after single-stage extraction.

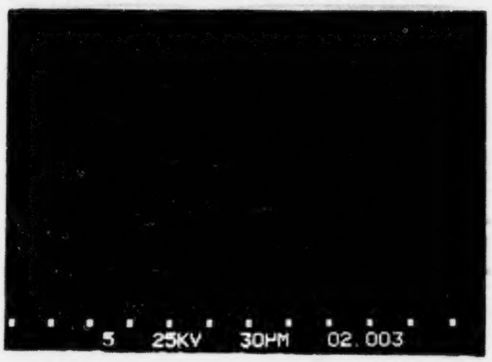

5 25KV 30µM 02.003

Figure 5. Distribution of $Ba_{k\alpha}$ in the region of Fig. 4.

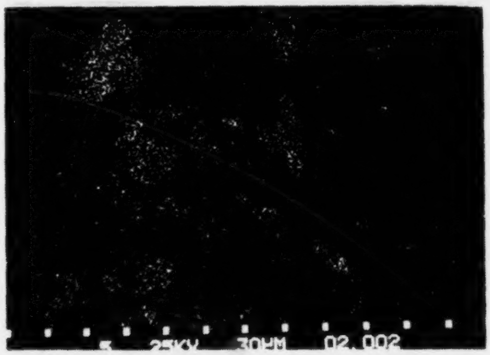

5 25KV 30µM 02.002

Figure 6. Distribution of $Fe_{k\alpha}$ in the region of Fig. 4.

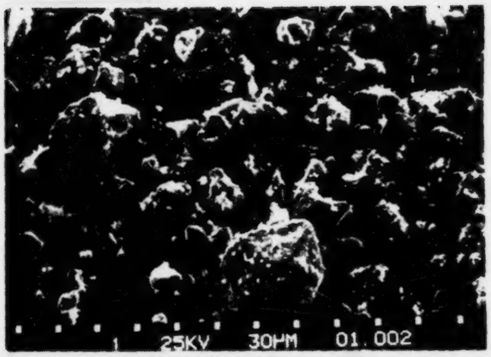

1 25KV 30µM 01.002

Figure 7. Backscattered electrons image of SH-960 salt waste after multi-stage extraction.

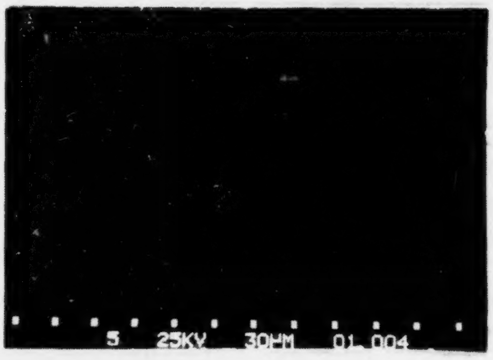

5 25KV 30µM 01.004

Figure 8. Distribution of $Ba_{k\alpha}$ in the region of Fig. 7.

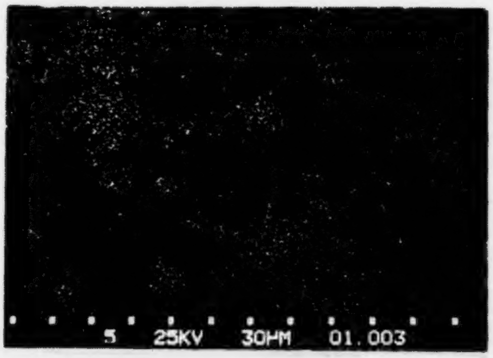

5 25KV 30µM 01.003

Figure 9. Distribution of $Fe_{k\alpha}$ in the region of Fig. 7.

chiometric doses, i.e.

0.744 g H_2SO_4/g Ba and

1.075 g Na_2SO_4/g Ba .

The disadvantage of using sulphuric acid is a strong acidification of the extract (pH 1.4) and of the water from barium sulphate rinsing (pH 2.4) .

The fine-crystalline barium sulphate sediment has a white colour and a water content of about 40.5 % after decantation of the post-reaction solution.

Rinsed barium sulphate contains insignificant amounts of impurities such as Sr, Si, Al, Ca and Na, but these occur at concentrations below the admissible levels for pure product.

Barium carbonate precipitation required application of sodium carbonate in 10 % excess with respect to the stoichiometric dose, i.e.

0.845 g Na_2CO_3/g Ba .

The major impurities found in the barium carbonate sediment are as follows: sodium carbonate (which can be removed to a large extent by rinsing) , strontium carbonate and calcium carbonate (both present in amounts below the admissible levels for pure product) . The water content of the barium carbonate sediment approached 75 %. The pH level in the effluent from precipitation was about 10, whereas that of the rinsing water ranged between 8.3 and 9.4.

The flow chart and mass balance of barium salt recovery is given in Figure 10.

Apart from the recovered product, i.e. barium sulphate or barium carbonate, both technological systems produce secondary pollutants which call for adequate treatment.

These are as follows:

- residues from water extraction, which take the form of fine-grained sediments containing predominantly very fine iron fillings and non-extracted barium (persisting in carbonate or oxide forms) . Wastes of that kind should be dewatered before they are stored on special dumping sites. Non-extracted barium may be recovered by dissolution in sulphuric acid with simultaneous precipitation of barium sulphate. Ferrous sulphate persisting in the solution can be recovered either by crystallization yielding $FeSO_4 \cdot 7\ H_2O$ or by precipitation with calcium hydroxide.

- brine produced during precipitation of barium sulphate or barium carbonate from the extract is practically impossible to remove by conventional methods. The only way to remove this pollutant is a controlled discharge of the solution into the sewer system. There may also be involved dilution with water from rinsing of the recovered barium salts. Some part of the rinsing water can be recirculated and reused for extraction (after discarding the first strongly polluted bath).

The investigations have shown that recovery of pure barium salts from spent SH-960 hardening salts is relatively easy to achieve. The amount of barium chloride used for the manufacture of hardening salts accounts for some 5 % of the total barium compounds used in Poland. Barite, the starting substance in the manufacture of barium compounds, is now being

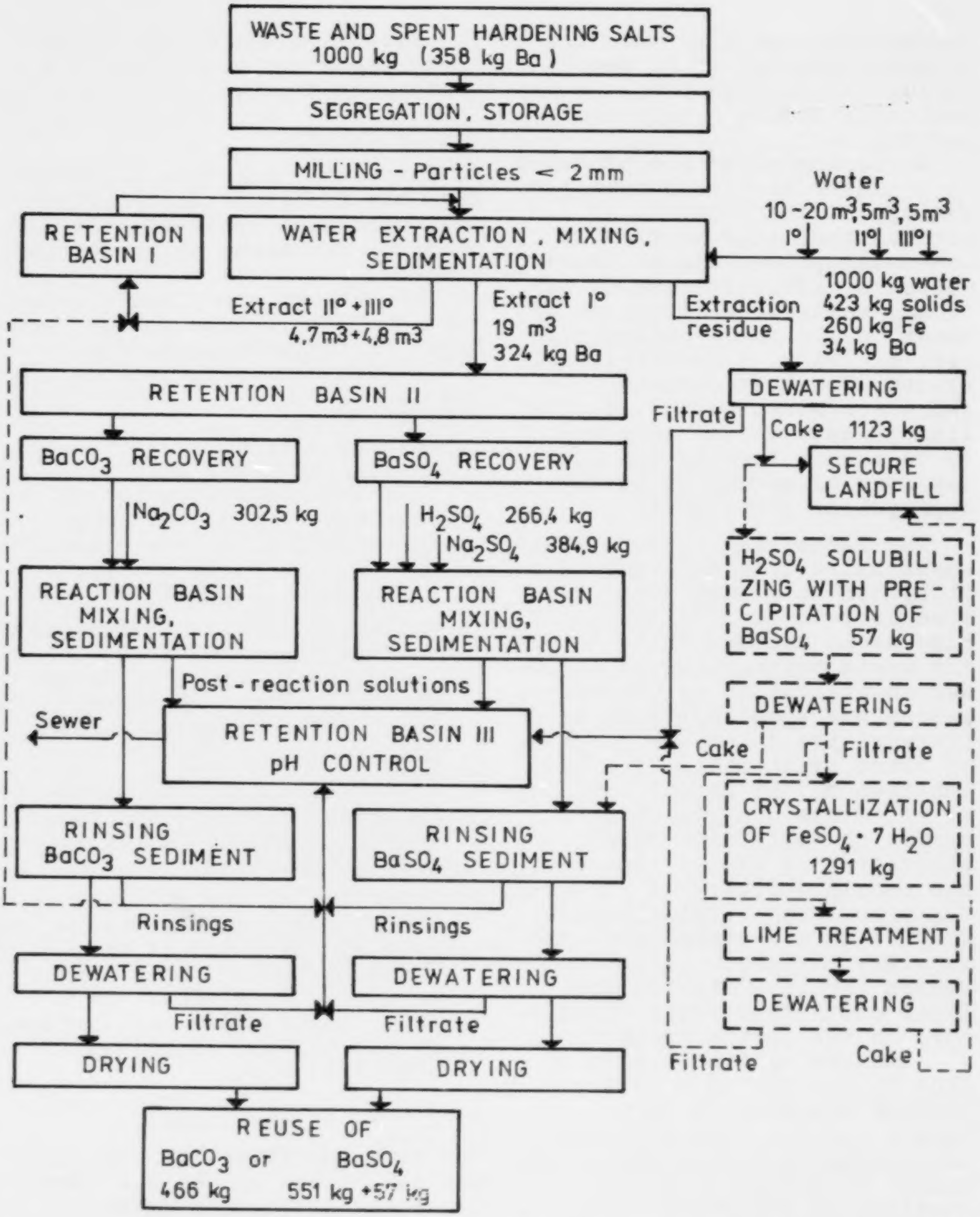

WASTE AND SPENT HARDENING SALTS
1000 kg (358 kg Ba)
SEGREGATION, STORAGE
MILLING - Particles < 2 mm
Water
10 - 20 m^3, 5 m^3, 5 m^3
I°
II°
III°
RETENTION BASIN I
WATER EXTRACTION, MIXING, SEDIMENTATION
Extract II° + III°
4,7 m3 + 4,8 m3
Extract I°
19 m^3
324 kg Ba
Extraction residue
1000 kg water
423 kg solids
260 kg Fe
34 kg Ba
RETENTION BASIN II
DEWATERING
Filtrate
Cake 1123 kg
SECURE LANDFILL
$BaCO_3$ RECOVERY
$BaSO_4$ RECOVERY
Na_2CO_3 302,5 kg
H_2SO_4 266,4 kg
Na_2SO_4 384,9 kg
H_2SO_4 SOLUBILIZING WITH PRECIPITATION OF $BaSO_4$ 57 kg
REACTION BASIN MIXING, SEDIMENTATION
REACTION BASIN MIXING, SEDIMENTATION
Post-reaction solutions
DEWATERING
Sewer
RETENTION BASIN III pH CONTROL
Cake
Filtrate
CRYSTALLIZATION OF $FeSO_4 \cdot 7H_2O$ 1291 kg
RINSING $BaCO_3$ SEDIMENT
RINSING $BaSO_4$ SEDIMENT
Rinsings
Rinsings
LIME TREATMENT
DEWATERING
DEWATERING
DEWATERING
Filtrate
Filtrate
Filtrate
Cake
DRYING
DRYING
REUSE OF
$BaCO_3$ or $BaSO_4$
466 kg 551 kg + 57 kg

Figure 10. SIMPLIFIED FLOW CHART AND MASS BALANCE OF BARIUM SALTS RECOVERY

partly imported from the free foreign-exchange zone. Hence, barium recovery from wastes may radically reduce a high-cost import.

Hardening salts are produced by a number of plants scattered throughout the country. It is obvious that this scattering makes the processing of those wastes a difficult task. A rational management of barium recovery calls for a nation-wide (or, at least, a macroregional) system. The most advantageous and the easiest method of utilizing waste barium compounds is to return them to the manufacturer of barium salts for appropriate processing.

The industrial plant wherein waste salts originate should be obligated to return these by free door-to-door delivery. It also seems recommendable to put the waste originating plant under an obligation to deliver wastes and spent salts as a prerequisite to enable purchase of brand fresh salts. The advantages may be as follows: more effective control of spent hardening salts management, maximization of barium recovery, and smooth delivery of wastes for processing. Preliminary analyses have revealed that the recovery of barium salts from wastes involves significantly lower costs than their manufacture on the barite basis.

Another alternative solution to the barium recovery problem consists in incorporating a special line for the processing of barium-containing wastes in the macroregional stations of hazardous waste management which are now under design.

The lanfilling of barium wastes is neither rational (when considering economic aspects) nor recommendable (when taking into account environmental pollution control) despite the fact that the direct landfilling costs are lower than the processing costs.

ACKNOWGLEMENTS

This study has been supported from the funds of the Institute of Environment Protection Engineering, Technical University of Wrocław.

The authors are greatly indebted to Lidia Pękalska, D.Sc. and Marek Maciejewski, D.Sc. for their valuable co-operation.

REFERENCES

1. Kempa, E., Szpadt, R., 1985, A Decision Model Resulting from the Classification of Hazardous Waste, In: Proc. Intern. Conf. on New Front. for Hazard. Waste Manag., Pittsburgh PA, pp. 171-178.
2. Müller, W., 1978, Aufarbeitung von Härtesalzrückständen. In: Materialien 2/78, Salze und salzhaltige Lösungen, Erich Schmidt Verlag Berlin, pp. 29-37.
3. Schenkel, W., 1983, Sonderabfallbeseitigung in der BRD, Wasser, Luft und Betrieb, Vol. 27, pp. 47-51
4. Sebastian, M. and R. Szpadt, 1986, Regeneration, Treatment and Disposal of the Spent Hardening Salts, Rep. of the Inst. of Env. Prot. Eng., Techn. Univ. of Wrocław, No SPR 44/86, (in Polish, unpublished).

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

ECONOMIC EVALUATION OF SOURCE REDUCTION PROJECTS

David Butler
Carl Fromm, P.E.
Christopher Timm, P.E.

Jacobs Engineering Group Inc.
251 South Lake Avenue
Pasadena, CA 91101

ABSTRACT

This paper examines costs and savings to a firm that are associated with source reduction projects. The types of operational costs impacted by such projects are identified and discussed with respect to their importance to capital project evaluation. Two examples of waste reduction projects are provided to illustrate the discussion.

INTRODUCTION

Recent legislative and regulatory emphasis on controlling the management of hazardous waste has escalated the current and anticipated future costs to firms of handling their process byproducts. According to The New York Times, the chemical waste management industry has entered a period of unprecedented growth and profit visibility, driven principally by government regulation (1). Management discussions in the annual reports of the larger chemical waste management firms indicate that these companies have very nearly a free hand in passing compliance costs on to customers in the form of higher prices (2). With no reasonable limit on waste management costs in sight, source reduction--the reduction of waste in-process--is becoming financially more attractive to companies in waste-generating industries.

This paper identifies types of operational costs and savings associated with source reduction projects and discusses their relative importance to capital project evaluation. Two case examples of waste reduction projects are provided to illustrate the discussion.

PURPOSE

This paper highlights operating costs that are impacted by source reduction projects. The methods of project evaluation are already well known. The intent of this discussion is to demonstrate the importance of incorporating these additional cost considerations into analyses of source reduction projects.

For this effort, information was drawn from the waste reduction audit experience of Jacobs Engineering.

APPROACH

Source reduction projects often have costs and savings different from those of other capital projects. In practice, the potential value of most capital projects has been established on the basis of savings in raw materials costs; savings in utilities, labor, and maintenance costs; and enhanced revenues through the creation of marketable byproducts. Source reduction projects can impact these same areas. However, the goal of reducing waste at the source focuses attention specifically on waste generation costs: disposal fees; fees/taxes on generators; waste transportation costs; on-site waste storage and handling costs; predisposal treatment costs; permitting, reporting, and recordkeeping costs; and pollution and safety liabilities. These costs were largely ignored in the past because the lack of an active governmental presence in environmental affairs allowed much smaller commitments of company resources to the waste management segment of company operations. Recent hazardous waste management requirements have caused these costs to increase beyond previous proportions.

For the purpose of evaluating a project to reduce waste quantities, some types of costs (savings) are larger and more easily quantified. These are disposal fees, transportation costs, predisposal treatment costs, raw materials costs, and operation and maintenance costs. These costs (savings) are usually considered first because they have a greater effect on project economics and involve less effort to estimate reliably. However, the other, "secondary" costs can gain importance depending on the type of project to be evaluated.

Two case examples were chosen to illustrate the role of easily quantified and less easily quantified costs in source reduction project evaluation. In each case, a fixed-price, fixed-dollar cash flow projection was constructed, which assumes no inflation and no change in the real relationships among costs. Inflation was netted out of interest rates per the Fisher formula (3). Fixed capital outlays were depreciated according to methods prescribed by recent federal tax legislation. All projects are assumed to begin construction on July 1, 1987. For each case, internal rate of return (IRR) and payback period (PBP) were used as measures of financial performance.

PROBLEMS ENCOUNTERED

A fixed-price cash flow projection ignores the effects that real changes in prices would have on project performance. For example, the avoided cost of waste disposal could rise against project operating costs in the future (both costs corrected for inflation), which would serve to enhance source reduction project performance. If avoided costs are expected to rise against operating costs in real terms, then fixed-price projections give conservative estimates of project performance because they understate the cash generation of the project. However, they do eliminate the uncertainty surrounding forecasts of future prices.

RESULTS

Case 1: Secondary Solvent Recovery

A resin-compounding operation at a pharmaceutical company uses 1,1,1-trichloroethane solvent for equipment cleaning. The present configuration uses a single-stage atmospheric still for solvent recovery. The still recovers 92 percent of the 3,455 lbs of spent solvent feed per day. The still bottoms, which contain 20 percent solids by weight, are sent to a TSD facility for solidification prior to landfilling.

The company is investigating the feasibility of adding a secondary recovery system to produce a nearly solvent-free, "dry" cake consisting of filler solids and polymerized resin. It is proposed that a scraped-drum evaporator be evaluated for this application. Spent solvent would be fed onto a heated drum as a thin coating. Solvent vapors would be collected and condensed into a receiver tank. The residue on the drum would be scraped off by a doctor blade resting on the drum surface and carried away for disposal. Design and construction of the system would require 3 months.

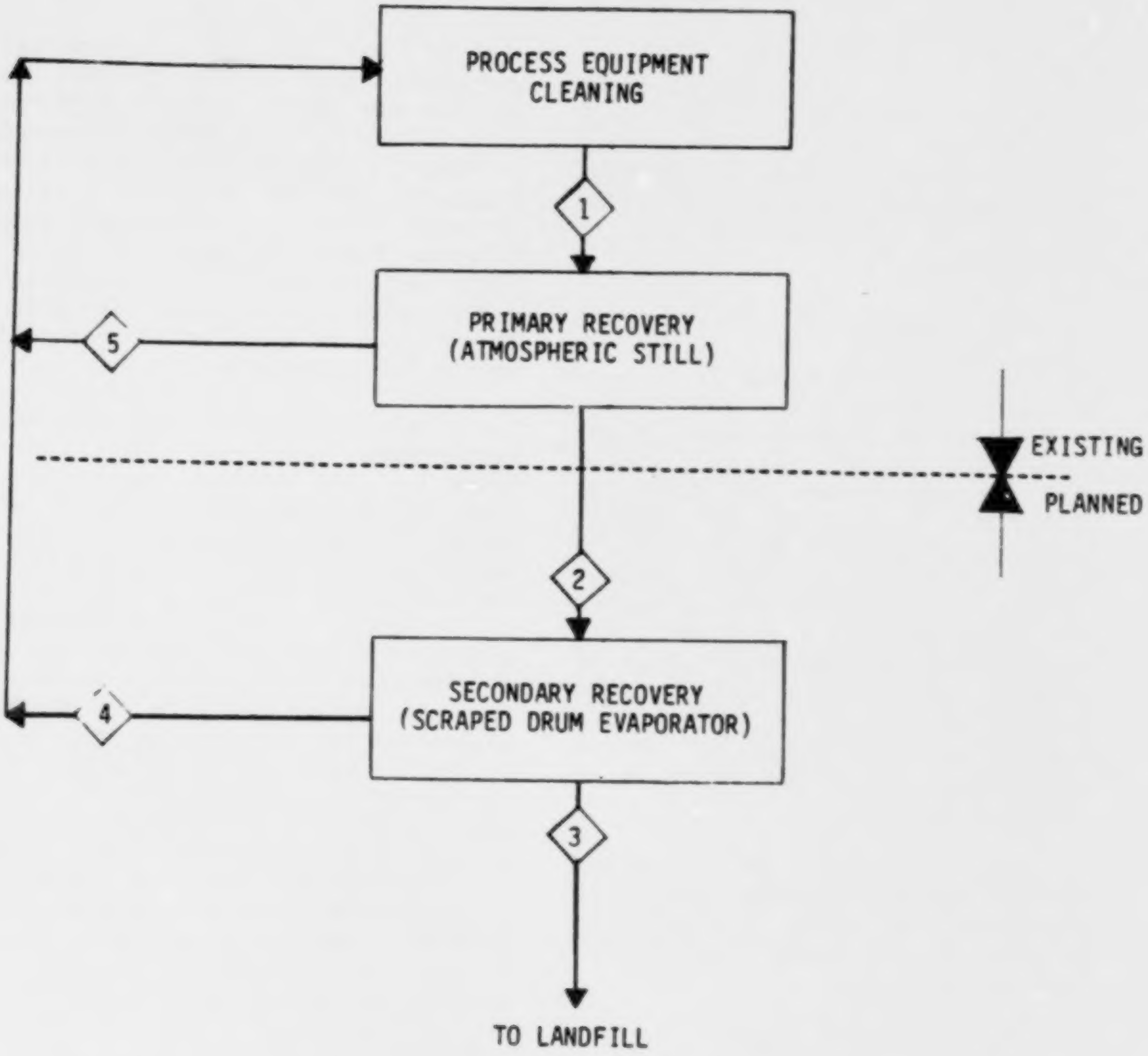
The current and proposed solvent recovery schemes, along with the associated mass balance, are depicted in the block flow diagram in Figure 1.

The estimated capital outlay, including an allowance for contingencies, is $69,450. Incremental operating cost is estimated at $12,340 per year. The value of raw material offset by the recovered solvent is $23,085. Avoided waste disposal cost is $12,770. Waste disposal cost is reduced both because there is less volume of waste and because the new byproduct is a solid rather than a liquid. The project is expected to require 3 months for implementation.

Table 1 reports the economic performance measures for this project. The internal rate of return for this project is calculated to be 32.37%. The project payback period is 3.3 years. To highlight the effect of avoided disposal cost on project economic performance, avoided disposal cost was removed in a subsequent evaluation. Internal rate of return fell to 8.37% and payback period was lengthened to 6.9 years. These would generally be considered as indications of poor performance. Therefore, the scraped-drum evaporator cannot be justified on the basis of recovered solvent alone. The presence of significant avoided disposal cost allows the scraped-drum evaporator project to be seriously considered as an alternative to continued solvent waste generation.

Table 1. Summary of Economic Performance Measures, Secondary Solvent Recovery

	Internal Rate of Return (%)	Payback Period (yrs)
Including Avoided Disposal Costs	32.37	3.3
Excluding Avoided Disposal Costs	8.37	6.9


PROCESS EQUIPMENT CLEANING
1
PRIMARY RECOVERY (ATMOSPHERIC STILL)
5
EXISTING
PLANNED
2
SECONDARY RECOVERY (SCRAPED DRUM EVAPORATOR)
4
3
TO LANDFILL

Stream	1	2	3	4	5
Solvent	3,455	270	27	243	3,185
Resin	30	30	30	0	0
Filler	76	76	76	0	0
Total, lbs/day	3,551	376	133	243	3,185

Figure 1. Block Flow Diagram and Mass Balance for Solvent Recovery System

Case 2: On-site Thermal Oxidation

A manufacturer of electronic components sends approximately 125,000 gallons per year of chlorinated and non-chlorinated solvent waste for off-site management. The cost of having the waste managed off-site has grown to nearly $250,000 per year, including disposal charges, taxes, and fees, and now represents a sizeable portion of manufacturing cost. The company is investigating ways to reduce this cost and is seriously considering on-site thermal oxidation.

Two configurations for a thermal oxidation system are proposed. The first, Alternative A, is a thermal oxidizer with a boiler for ancillary heat recovery. Alternative B is a thermal oxidizer alone. Each system would burn only non-chlorinated solvents, which comprise somewhat more than 90 percent of the facility's total solvent waste generation.

Total capital outlay is estimated at $560,300 for Alternative A, $143,000 of which is estimated permitting cost. Alternative A would require 1 year to build and permit. The outlay for Alternative B is estimated at $658,000, of which $328,000 is permitting cost. The reason for the difference in permitting costs is that Alternative A, because of its provision for heat recovery, can be permitted as a resource recovery facility, whereas Alternative B must be permitted as a hazardous waste incinerator. Alternative B is expected to require 2.5 years to construct and permit. Table 2 displays the breakdown of the permitting cost estimates. The midpoints of the cost ranges were used in the economic feasibility analysis.

To establish a benchmark for comparison, the alternatives were first evaluated without permitting costs. The permitting costs were subsequently added to the capital outlay amounts and the alternatives were reevaluated.

Table 3 shows the result of this evaluation. Without permitting costs, both alternatives exhibit unexceptional economic performance with regard to internal rate of return, and each is outside manufacturing industry norms for payback period of 2-3 years maximum. When permitting costs are included, the projected performance of each project is reduced substantially, though Alternative A still exhibits average economic performance. In the case of Alternative B, the payback period has more than doubled.

It should be noted that Alternative B is expected to require 1.5 years longer to permit than Alternative A. The permitting costs in Table 1 do not include the cost of this delay to the company if it chooses Alternative B. To approximate the consequence of implementing Alternative B over Alternative A in this instance, the cost of disposal during the additional 1.5 years is entered into the operating cash flows for Alternative B. The result is an internal rate of return of 3.81% and a payback period of 12.1 years. These figures are more useful for evaluating incineration alone against incineration with heat recovery in this instance.

Summary and Conclusion

The costs of waste generation are no longer a negligible part of overall operating cost. Two cases have been outlined where waste generation costs figure importantly in

Table 2. Permitting Costs Associated with the Thermal Oxidizer

	Resource Recovery Facility	Hazardous Waste Incinerator
1. Prepare Part B Application	$ 25,000	$ 25,000
2. Agency Review and Response to Notice of Deficiencies	$ 4,000-10,000	$ 10,000-16,000
3. Trial Burn Plan		$ 15,000-30,000
4. Formal Trial Burn		$ 55,000-200,000 depending on number of tests required.
5. Test Burn in Lieu of Formal Trial Burn	$ 15,000-30,000	--
6. Public Hearings/Community Awareness/Local Permitting	$ 30,000 (a)	$ 50,000 (a)
7. Risk Assessment (if required)	$ 40,000 max	$ 25,000-40,000
Subtotal	$ 74,000-135,000	$155,000-361,000
8. Contingency for Permitting Uncertainties	$ 23,000	$ 54,000
9. Optional Additional Monitoring Instrumentation Costs	$ 12,000 max	$ 12,000 max
10. State Agency Permitting Cost	$ 10,000	$ 10,000
TOTAL	$107,000-180,000	$219,000-437,000

project evaluation. In the first case, the magnitude of avoided disposal cost supports secondary solvent recovery. In the second case, each project alternative involves significant avoided disposal cost, but the costs and delays associated with permitting a hazardous waste incinerator clearly eliminate incineration alone as an option for on-site waste management.

These two cases also serve to indicate how recent regulation has enhanced the economics of source reduction. Both projects stand on the basis of avoided disposal cost. By changing the relative prices associated with waste generation and management, regulation has encouraged firms to implement source reduction measures in order to maintain production cost efficiency. It is apparent that source reduction in many cases could represent a lower-cost alternative to continued waste generation.

NOTES AND REFERENCES

1. Wiggins, P., "Waste Control: Strong Outlook," The New York Times, September 8, 1986.

2. See, for example, Waste Management Inc., 1985 Annual Report, p. 51: "Competitive conditions and governmental regulations permitting, the Company expects to adjust its prices to recognize future cost increases." See also International Technol-

Table 3. Summary of Costs and Benefits, On-site Thermal Oxidation

	Alternative A	Alternative B
Benefits		
Recovered Heat	43,400	--
Avoided Disposal Cost	185,360	185,360
Total Benefits	228,760	185,360
Operating costs		
Raw Materials & Utilities	6,394	6,314
Overhead	27,000	18,000
Operating & Maintenance Labor	52,412	36,920
Insurance & Property Taxes	13,562	10,725
Total Operating Costs	99,368	71,959
Performance without Permitting Costs		
Internal Rate of Return (%)	22.45	17.54
Payback Period (yrs)	3.9	3.9
Performance with Permitting Costs		
Internal Rate of Return (%)	15.99	7.70
Payback Period (hrs)	5.5	8.4

ogy Corporation's 1986 Annual Report, p. 16: "The substantial costs associated with (a major investment program for complying with the new RCRA requirements), coupled with increased taxation on waste disposal, has resulted in substantial periodic price increases. These are expected to continue as new regulations impose more stringment pretreatment standards on disposal to landfill."

3. $(1 + r) = (1 + i)/(1 + n)$, where
   r = real interest rate
   i = nominal interest rate
   n = rate of inflation

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

MINIMIZATION OF SOLVENT WASTES FROM AN ELECTRONIC CAPACITOR MANUFACTURING PROCESS

Harry M. Freeman
Hazardous Waste Engineering
Research Laboratory
Cincinnati, Ohio 45268

James R. Teuscher
SFE Technologies, Inc.
San Fernando, CA 91340

Michael S. Callahan
Jacobs Engineering Group Inc.
Pasadena, CA 91101

Carl H. Fromm
Jacobs Engineering Group Inc.
Pasadena, CA 91101

ABSTRACT

The paper summarizes the results and recommendations of a waste minimization audit carried out to identify opportunities for reducing solvent wastes from an electronic capacitor manufacturing process. The major solvent waste generating operations audited included the cleaning of various equipment with RM-513 (a proprietary solvent) and with recycled 1,1,1-trichlorethane (TCA); general cleaning with isopropyl alcohol and with recycled TCA; and the on-site recovery of spent TCA. The audit resulted in 22 waste reduction options being postulated and seven selected for further investigation. This paper is extracted from the EPA report, Case Studies of Minimization of Solvent Waste from Parts Cleaning and from Electronic Capacitor Manufacture Operations presently under review for clearance from HWERL.

INTRODUCTION AND PURPOSE

In order to increase the acceptance of waste minimization by industrial hazardous waste generators, the EPA has supported the development of a procedure for facilitating identification of opportunities for waste reduction.

The general procedure is summarized in Table 1. (A manual based on the procedure is currently under preparation by the EPA. The manual will be available from HWERL, Cincinnati in the fall of 1987). The case study summarized in this paper was one of five such studies carried out to test the auditing procedure. The work described was performed in the fall of 1986.

APPROACH

The facility chosen for the study is a major manufacturer of multilayer ceramic capacitors used primarily by the telecommunications and military electronics industries. Production operations are performed in two separate buildings located within close proximity to each other. Ceramic materials are formulated in an Annex building and then transferred to the Main Facility where the capacitors are formed. Various finishing operations are performed at both buildings.

Preceding page blank

Table 1. Recommended Waste Minimization Audit Procedure

Program Phase	Activities	Product
Pre-Audit	1. Preparation for the audit	o needs list/inspection agenda
	2. Pre-audit meeting and inspection	o notes
	3. Data compilation and waste stream selection	o facility and process description o waste description o rationale for selection
Audit	4. Facility inspection	o notes
	5. Generation of a comprehensive set of WM options	o list of proposed options with written rationale
	6. Options evaluation	o independent options ratings by audit team and by plant personnel followed by joint review
	7. Selection of options for feasibility analyses	o list of selected options o options interim report
Post-Audit	8. Technical and economic feasibility analysis	o study or budget grade estimates of capital and operating costs; profitability analysis
	9. Final report preparation	o final report with recommendations

Major operations are depicted schematically in the block flow diagram (Figure 1).

The solvent wastes are generated mainly by various equipment cleaning operations:

- o ball mill cleaning and off-spec slurry disposal;
- o cleaning of the transfer pots;
- o off-spec slurry disposal, cleaning and flushing of the slurry application system;
- o general cleaning;
- o still bottoms from the on-site TCA still.

The most common solvents used for cleaning include 1,1,1-trichlorethane (TCA), RM-513 (a proprietary solvent), and isopropyl alcohol (IPA).

Development and Screening of Solvent Waste Minimization Options

Each main solvent cleaning operation was scrutinized by the audit team so as to develop a list of options that would reduce or eliminate waste generation at source. The focus was mainly on recycling of spent cleaning solvent; such approach was deemed as the most effective short-term option. The long-term solutions (e.g. development of non-solvent formulations) could not be meaningfully addressed in this study.

Table 2 lists the various waste minimization options identified by the audit team for each operation. For initial screening, each option was rated on a scale of zero (low) to ten (high) for its waste reduction effectiveness, extent of current use, and future application potential. After rating each option, the current and future reduction indices were determined.

Following discussion with facility personnel, several of the options described above were selected for further investigation based on their high future reduction index. The options evaluated in further detail were:

- o Ball Mill and Slurry Application Wastes: Segregate and recycle RM-513 based off-spec slurry.
- o Ball Mill, Transfer Pots, and Slurry Application Wastes: Segregate, standardize, and recycle cleaning solvents.
- o Slurry Application Wastes: Segregate and recycle RM-513 flushing solvent.
- o Slurry Application Wastes: Convert application system filters to bag/wire mesh type.
- o General Cleaning Wastes: Segregate and recycle isopropyl alcohol waste.
- o TCA Primary Recovery Wastes: Install secondary recovery system.

Figure 2 partially depicts a proposed scheme for segregation and recycle of cleaning solvents based on the options indicated. Paragraphs below detail the results of feasibility analysis performed for each option.

Ball Mill/Slurry Application Wastes

By segregating the off-spec slurry waste from the other wastes generated at the ball mill and slurry application operations, 20 gallons per week of RM-513 waste would be rendered recyclable. Segregation would require that separate storage containers be provided to the operators. Proper training of the operators to use the special storage containers should not be a problem, since the facility has recently implemented a successful waste segregation program.

Once this waste is segregated, a small 55-gallon batch distillation unit could be procured for the recovery of RM-513). The cost of procuring and installing an automated still is estimated to be $25,750. Annual savings based on recovering 14.4 gallons of solvent per week and reducing waste disposal costs would amount to $6,040. This equates to a payback period of 4.3 years. Since this period exceeds the required hurdle rate of 3.0 years, procurement of a still to recycle this waste stream alone cannot be justified.

Ball Mill/Transfer Pots/Slurry Application Wastes

After segregating the wastes according to solvent type (RM-513 or TCA), efforts should be made to standardize the type of solvent used for cleaning. Figure 2 presents a modified block flow diagram for standardizing the solvent used for cleaning the equipment which handles RM-513 based materials. The following major changes to the currently employed cleaning scheme are proposed:

- o Primary ball mill rinse would use RM-513, instead of TCA.
- o Primary transfer pot cleaning would use RM-513, instead of TCA.
- o Slurry application pot rinsing would use RM-513, instead of TCA.

Once these changes are made, the amount of RM-513 based waste will increase so that the economic justification for procuring a still is improved. Assuming that all 50 gallons per week of waste can be converted to RM-513 based waste, annual savings of $19,130 would result. This equates to an acceptable payback period of 1.3 years.

Slurry Application Wastes - Solvent Flush

By segregating the flushing waste from the other wastes that are sent off-site for incineration, 14.5 gallons per week of RM-513 could be recovered by use of a small batch still. The cost of procuring and installing an automated still is estimated to be $25,750. Annual savings based on recovering RM-513 and reducing waste disposal costs would amount to $5,400. This equates to a payback period of 4.8 years which makes this option, by itself, economically infeasible.

Slurry Application Wastes - Filter Cartridges

Waste containing spent cartridge spent filters could be virtually eliminated by changing to a wire mesh filter. A major advantage of this style of filter is that it is reusable and that no filter housing replacement would be necessary. The envisioned system would consist of replacing the current filters (4 per system) with washable wire mesh filters and adding a few valves to allow for backwashing of the filters with the solvent used for system flushing. Based on a total installed cost of $9,830 for all six systems, the annual savings would amount to $6,660. This equates to a payback period of 1.5 years, making this a viable option.

General Cleaning Wastes - Isopropyl Alcohol

General facility cleaning generates 94 gallons per week of dirty isopropyl alcohol (IPA). Since the overall quality of this waste is unknown, it is assumed that only 50 percent of the waste would be amenable to recycling. The remaining 50 percent (assumed to be too heavily contaminated to allow for efficient recovery), would continue to be sent off-site for incineration. Included with this waste would be the still bottoms from IPA recovery.

Recycling of IPA waste is estimated to save the facility $11,650 per year. Based on a total installed cost of $25,750, the resulting payback period is 2.2 years. Since this is less than the required hurdle rate of 3.0 years, and since it was conservatively assumed that only 50 percent of the waste was recyclable, this option is considered viable. For IPA waste that was too heavily contaminated with water to allow for recycling, drying with unslaked lime could be performed. While this would increase the amount of recyclable IPA, the effects of increased solids disposal would have to be addressed.

TCA Primary Recovery Wastes

The facility currently generates 55 gallons per week of still bottoms from the operation of their TCA primary recovery system. This waste is sent off-site for additional recovery of TCA (estimated to be 65 percent). Use of an on-site still that could achieve a secondary recovery of 80 percent would reduce annual costs by $7,100. Based on a total installed cost of $25,750 for a still, the resulting payback period is 3.6 years.

In addition to the marginal economic performance, the residuals (distillation bottoms) may pose disposal problems after November 8, 1986 if the TCA level exceeds 10,000 ppm. It is recommended that the solvent content of residuals be determined experimentally before the secondary recovery of the still bottoms is attempted on a larger scale.

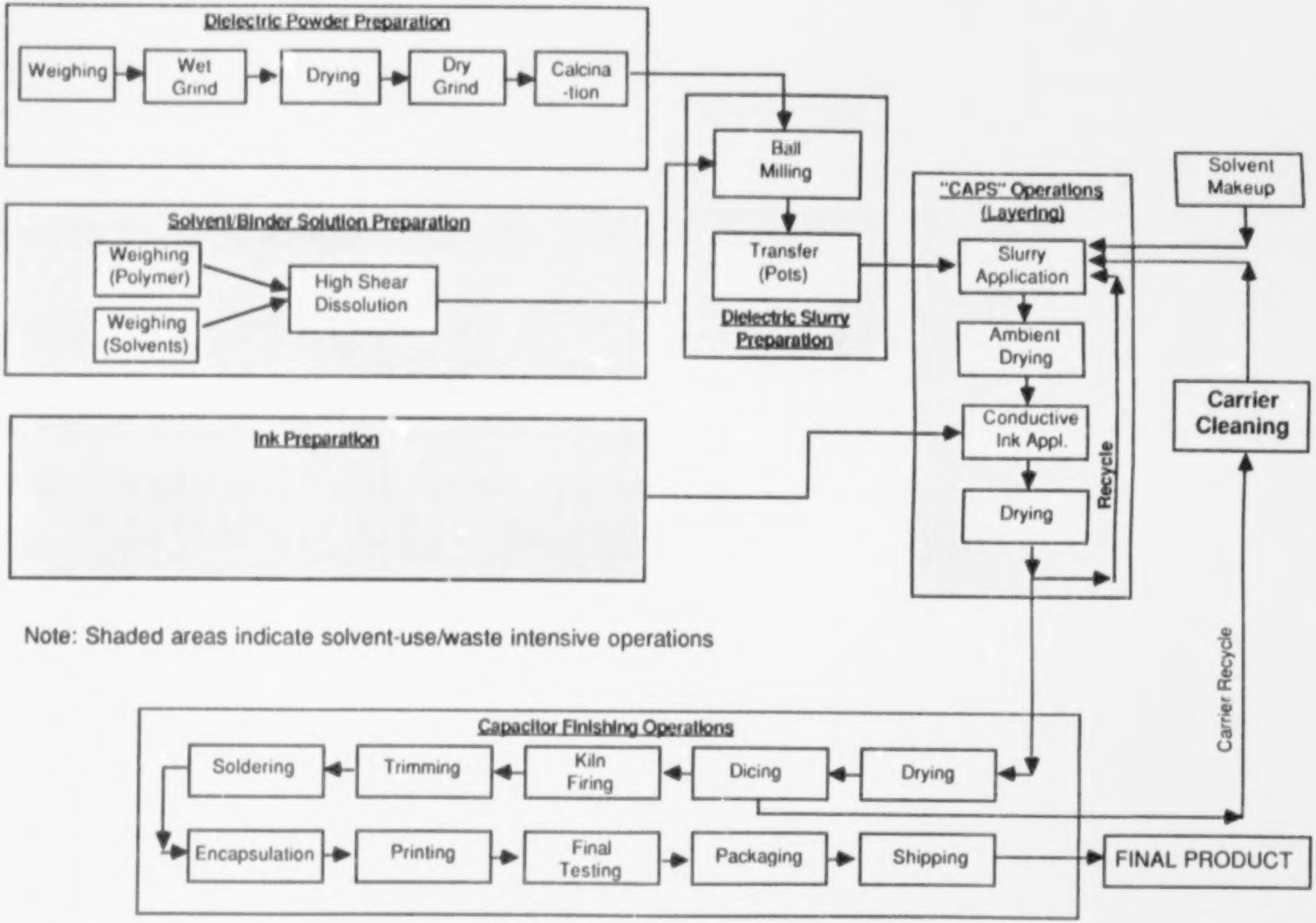
SUMMARY

Five major solvent waste producing operations were investigated during the initial audit. The five operations involved ball milling, slurry transfer pot cleaning, cleaning of the slurry application systems, general cleaning performed throughout the facility, and operation of the on-site TCA still. Waste minimization options were formulated for each operation, with the main focus placed on ways to increase the recyclability of the waste produced. These options were then tabulated and rated. From these ratings, options were selected for additional economic analysis. The results of this analysis are shown in Table 3.

Many of the options discussed above rely on the use of a small batch still for solvent recovery. Since the still operates in a batch mode, all of these waste streams can be separately processed in the same unit. By dividing the capital cost for one system by the savings resulting from implementation of the four options indicated in Table 3, the overall payback period is calculated at 0.9 years, as opposed to periods ranging from 2.2 to 4.8 years for each option individually. By incorporation of the above-mentioned measures, the facility can reduce solvent waste generation by 54 percent (5,810 gallons per year) at an estimated annual savings of $30,190. In summary, the economic and technical feasibility for on-site reclamation of cleaning solvent is demonstrated.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.


Dielectric Powder Preparation
Weighing
Wet Grind
Drying
Dry Grind
Calcina -tion
Solvent/Binder Solution Preparation
Weighing (Polymer)
Weighing (Solvents)
High Shear Dissolution
Ink Preparation
Ball Milling
Transfer (Pots)
Dielectric Slurry Preparation
"CAPS" Operations (Layering)
Slurry Application
Ambient Drying
Conductive Ink Appl.
Drying
Recycle
Solvent Makeup
Carrier Cleaning
Carrier Recycle
Capacitor Finishing Operations
Drying
Dicing
Kiln Firing
Trimming
Soldering
Encapsulation
Printing
Final Testing
Packaging
Shipping
FINAL PRODUCT

Note: Shaded areas indicate solvent-use/waste intensive operations

Figure 1. Block Flow Diagram for Ceramic Capacitor "CAPS" Manufacturing Process.

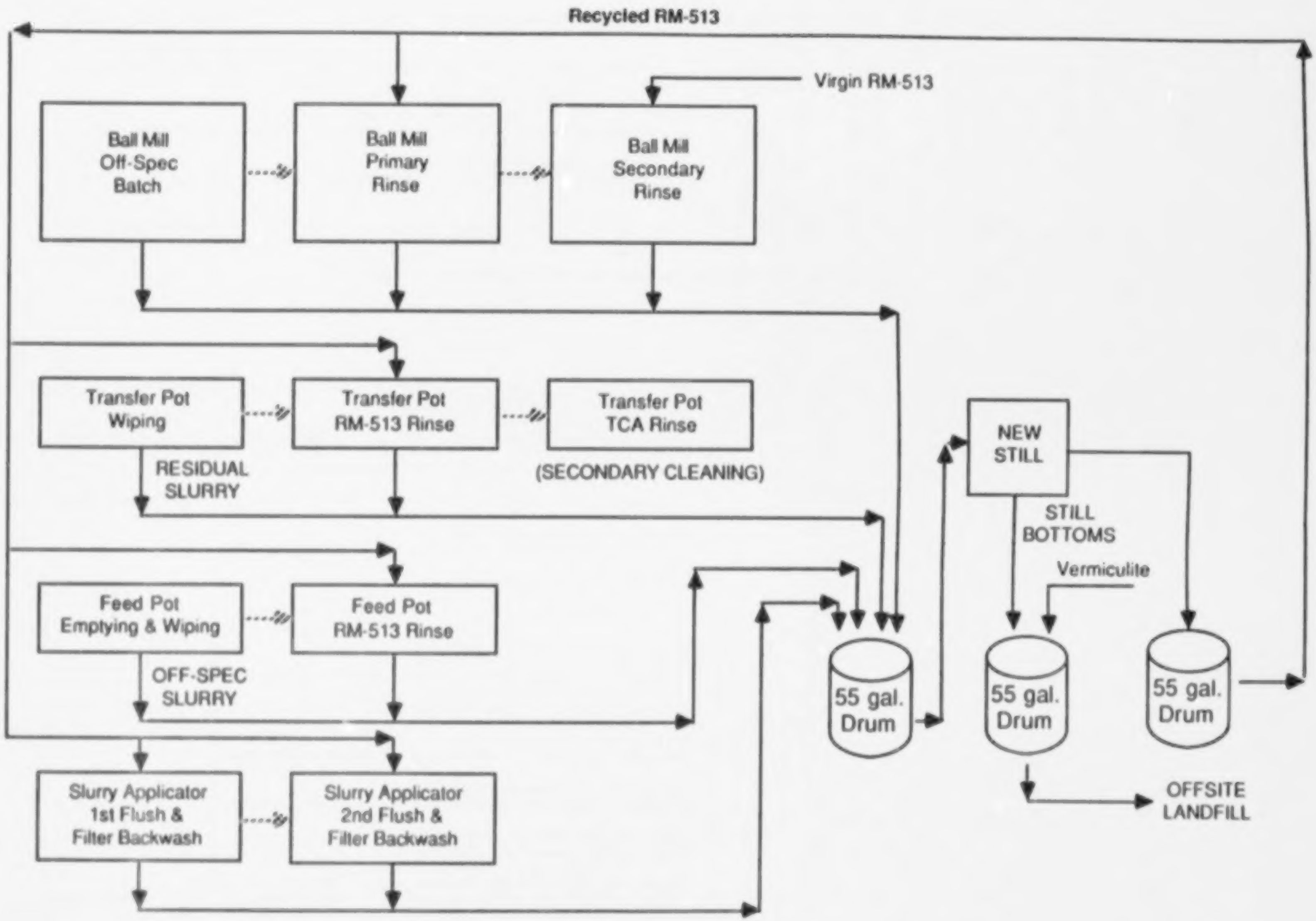

Recycled RM-513
Virgin RM-513
Ball Mill Off-Spec Batch
Ball Mill Primary Rinse
Ball Mill Secondary Rinse
Transfer Pot Wiping
Transfer Pot RM-513 Rinse
Transfer Pot TCA Rinse
RESIDUAL SLURRY
(SECONDARY CLEANING)
Feed Pot Emptying & Wiping
Feed Pot RM-513 Rinse
OFF-SPEC SLURRY
Slurry Applicator 1st Flush & Filter Backwash
Slurry Applicator 2nd Flush & Filter Backwash
55 gal. Drum
NEW STILL
STILL BOTTOMS
Vermiculite
55 gal. Drum
55 gal. Drum
OFFSITE LANDFILL

Figure 2. Proposed RM-513 Cleaning Solvent Recycle System.

TABLE 2. SUMMARY OF POSTULATED SOLVENT WASTE MINIMIZATION OPTIONS

Waste Source	Waste	Control Methodology	Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Current Reduction Index	Future Reduction Index
Ball Mills	Off-Spec Slurry Mill Cleaning	1. Dedicate mills to slurry formula.	8	9	5	7	0
		2. Increase degree of quality control.	8	8	5	6	1
		3. Use two-step mill flush.	5	5	7	3	2
		4. Segregate and recycle RM-513 wastes.	6	0	8	0	5
		5. Standardize solvent used and recycle.	9	0	7	0	===> 6
Transfer Pots	Primary Cleaning	1. Wipe transfer pot before solvent use.	4	8	5	3	0
		2. Segregate, standardize, and recycle.	9	0	8	0	===> 7
	Secondary Cleaning	3. Reduce evaporative loss of solvent.	1	6	5	1	0
		4. Increase solvent cleaning efficiency.	6	8	4	5	0
Slurry Application System	Off-Spec Slurry	1. Increase degree of quality control.	8	8	5	6	1
	Feed Pot Cleaning	2. Wipe feed pot before solvent use.	4	6	7	2	1
		3. Segregate and recycle RM-513 wastes.	7	0	8	0	6
		4. Segregate, standardize, and recycle.	9	0	7	0	===> 6
	System Flushing	5. Use two-step flush sequence.	5	0	7	0	4
	Filter Changing	6. Use bag/metal mesh type filters.	7	0	7	0	5
	Carrier Cleaning	7. Reduce evaporative loss of solvent.	1	6	5	1	0
		8. Increase solvent cleaning efficiency.	6	8	4	5	0
General Cleaning	Isopropyl Alcohol	1. Segregate and recycle solvent waste.	5	0	8	0	===> 4
	111 Trichloroethane	2. Segregate and recycle solvent waste.	9	9	9	8	1
On-Site TCA Still	Still Bottoms	1. Wipe pots before solvent cleaning.	4	9	5	4	0
		2. Maintain the solvent's recyclability.	9	7	6	6	2
		3. Install a secondary recovery system.	5	0	8	0	===> 4

TABLE 3. SUMMARY OF SOLVENT WASTE MINIMIZATION OPTIONS ANALYZED

Waste Source	Minimization Option	Waste Reduction gallons/year	Waste Reduction percent	Net Annual Savings(f)	Capital Costs	Payback Years(g)
Ball Mills and Transfer Pots	(*) Segregate and recycle RM-513 wastes.	720	28.8	$6,040	$25,750	4.3
	Standardize solvent used and recycle.	2,150	86.0	$19,130	$25,750	1.3
Slurry Application Systems	(*) Segregate and recycle cleaning waste.	725	96.7	$5,400	$25,750	4.8
	Use bag type filters.	---	90.0	$1,260	$23,950	19.0
	Use metal mesh type filters.	---	100.0	$6,660	$9,830	1.5
General Cleaning With Isopropyl Alcohol	(*) Segregate and recycle cleaning waste.	2,350	50.0	$11,650	$25,750	2.2
TCA Primary Recovery	(*) Install a secondary recovery system.	2,015	73.3	$7,100	$25,750	3.6
All Waste Sources Shown Above	Use a common batch still for (*) methods.	5,810	54.3	$30,190	$25,750	0.9

SELECTION OF A MOBILE INCINERATION SYSTEM

John C. Reed
Steven R. Strauss
James D. Cobb

Illinois Environmental Protection Agency
Springfield, Illinois 62794-9276

ABSTRACT

Recognizing the need to develop a mobile incineration technology in the State of Illinois, the Illinois Environmental Protection Agency ("IEPA" or "Agency") formed an inter-Agency task force in 1984 consisting of members from the divisions of Land Pollution Control, Air Pollution Control and the Office of Chemical Safety. A series of meetings with interest contractors was initiated, site visits were held, a Request for Qualifications was issued and in the latter part of 1985, a Request for Proposal ("RFP") for a Remedial Action utilizing a mobile incineration system was issued by the Agency. After a thorough evaluation of the proposals submitted, a contract was awarded to Roy F. Weston, Inc. to mobilize a mobile incineration system at a designated site and conduct remediation activities. The unit was mobilized in May of 1987 and treatment of contaminated soils is expected to be completed by the end of 1987.

This paper describes the background of the selection of the mobile incineration technology as it has been developed by the IEPA. In the course of this selection process, IEPA has developed evaluation tools and techniques that will be useful to others involved in hazardous waste cleanups. The IEPA believes that the information and methods described here will ensure the selection of the best treatment system with the lowest probability of foreseeable difficulties.

INTRODUCTION

For many years, the most common practice for disposing of hazardous substances was dumping into available landfills. Now, the need for technological alternatives to landfills is well recognized. This need has become more acute with the advent of the Comprehensive Environmental Response, Compensation and Liability Act, the discovery of many nonpermitted treatment, storage and disposal facilities requiring remediation of significant amounts of contaminated soil, sludge and liquids, and the enactment in Illinois of a legislative mandate requiring that hazardous waste streams may be landfilled only after a demonstration has been made that recycling, incineration or chemical, physical or biological treatment of the waste is not technologically feasible or economically reasonable (1).Incineration and other means of thermal destruction have been well accepted as attractive alternatives for disposing of hazardous substances but are costly and suffer from the "NIMBY" (not in my backyard) syndrome. Thus, the concept of a mobile incineration system that can be transported from one hazardous waste site to another becomes very attractive. The hazardous substances can be treated on site, thereby avoiding the necessity for transport of the waste to a stationary incineration facility or landfill; the unit is on site for a limited period of time correcting a known problem and then moved, thereby avoiding the public resistance to a stationary facility; the stationary incinerator facilities are not backlogged by a deluge of hazardous substances emanating from a hazardous waste cleanup (often between 7000 and 15,000 tons of contaminated materials) and the cost of treatment of the waste on site with a mobile incineration system appears to be significantly less than transportation and treatment of waste to a stationary incineration facility.

ORIGINAL CONCEPT

Stationary incineration has been long considered an adequate disposal technology and many units have been built and operated (2). The original concept of mobile incineration technology was first actively investigated by the USEPA in Edison, N.J. with a trailer-mounted rotary kiln (3).

The first field test of USEPA's mobile incineration system was at the Denney Farm site in southwest Missouri (McDowell, Missouri)(3). This field test gives a guide to the various problems that can be encountered by a mobile incinerator and has been very helpful in the Agency's own evaluation of the process.

BACKGROUND OF SELECTION PROCESS

The early background of the selection process has been described in a previous paper (4). In October, 1984, a task force was formed at the IEPA consisting of the divisions of Land Pollution Control, Air Pollution Control and the Office of Chemical Safety to consider the feasibility and appropriate technology for alternate treatment technology at Superfund and "Clean Illinois" sites. "Clean Illinois" is a state-funded program analogous to the Superfund Program at the federal level.

As a result of these efforts in October, 1985, a Request for Proposal ("RFP") to remediate a specific site in Illinois utilizing a mobile incineration system was issued to prospective bidders. The site proposed for remediation was an abandoned salvage yard containing approximately 7000 tons of soils contaminated with polychlorinated biphenyls in concentrations up to 1650 PPM. Six bidders responded to the RFP by submitting proposals to the Agency.

EVALUATION FORMAT

An evaluation committee was selected to evaluate the proposals submitted in response to the RFP. The evaluation committee consisted of members from the Divisions of Land Pollution Control and Air Pollution Control as well as a consultant from a large private engineering company having substantial on-hands experience with incineration technology. The committee evaluated the technical adequacy of the incineration system, the proposed methodology for accomplishing the scope of work, and the permitting experience of the bidders. In addition, inasmuch as the RFP requested a turn-key type of proposal, the Agency anticipated the bidders being composed of a composite group, consisting of an incinerator manufacturer/fabricator, an earth moving remediation contractor and an engineering company with permitting experience. Accordingly, the organization of the bidder and the cohesiveness of the proposal were evaluated. An evaluation form was designed to thoroughly examine the above described components of the bidder's proposals.

TECHNOLOGY OF THE MOBILE INCINERATION SYSTEM

The IEPA wanted as much assurance as possible that the incineration system ultimately chosen would have a high likelihood of success in the field. Accordingly, the system had to be designed to meet or exceed the performance standards established by the Toxic Substances Control Act (TSCA) for incineration of PCB's as well as performance and operating standards established by the Air and Land Divisions of the Agency. Process flow diagrams and process and instrumentation diagrams as well as lengthy narratives were evaluated to determine the capabilities of the proposed systems.

The proposed control room of each bidder was evaluated to be certain monitoring with continuous data recording would be done for the parameters deemed essential by the Agency, as well as contain an automatic control system and shut off system when operations of the incinerator failed to meet acceptable temperature and stack gas concentrations. Additionally, the waste capacity of the system and backup and redundancy of the system were evaluated. The Air Pollution Control equipment was evaluated utilizing descriptions, specifications and drawings. Air monitoring procedures and equipment were evaluated. The evaluation committee also evaluated how the proposals dealt with problems that had arisen in the USEPA field test (4) such as carryover of ash into the secondary and combustion controls to assure proper and complete combustion.

The major technical disparities among the proposals were the level of sophistication of the proposed control rooms, vertical afterburners versus horizontal afterburners, wet scrubbers versus dry scrubbers, waste throughput capacities, energy efficiencies of the systems and the types of air pollution control equipment.

SCOPE OF WORK

The bidder's proposed methodology to implement the required work was evaluated. Sampling techniques, laboratory facilities, excavation techniques, dust suppression techniques, runoff control, treatment and disposal of waste water and ambient air monitoring were evaluated. The type of variations within the proposals dealt with such issues as the extent of soil sampling necessary at the excavation areas, extent of sampling necessary of the ash residues and the method of analysis of both feed soils and ash residues. Also, there were variations in extent of ambient air monitoring necessary to detect particulate and organic emissions.

Based upon the difficulty encountered in evaluating certain of the above criteria, the IEPA concluded that the proposals would have been more amenable to comparison in certain areas if the RFP had contained more specificity. In addition, where federal approval is necessary in the permitting process, such as TSCA, engaging in a dialogue with federal officials early in the process as to federal requirements would have helped facilitate the evaluation and contracting process.

After the initial evaluation, each of the bidders was given an opportunity to make a presentation of their proposal to the evaluation committee. The meetings gave the evaluators an opportunity to ask the bidders questions concerning the bidders' proposals and receive needed clarification. In addition, the bidders had the opportunity to meet the evaluation committee and to accentuate these portions of the proposal they felt the most important. Finally, it provided the evaluation committee an opportunity to inquire and discuss with the bidders the types of unforeseen circumstances that might occur at the site which would cause delays and cost adjustments. Issues affecting the time schedules and cost proposals of the bidders were the availability of an adequate fuel source, availability of sufficient quantity of water of requisite quality, excavating into the ground water table, high moisture content soils necessitating higher residence time, high or low BTU soils affecting throughput in the system, potential of contamination of the field laboratory and the advent of winter weather.

At the conclusion of the oral presentation, the bidders were given an opportunity to submit clarifications to their proposals which were discussed during the presentations and their "last best" bid, at which time the bidders had the opportunity to alter the cost proposal portion of their proposals.

The evaluation committee then went through the score sheet a final time to deal with any changes in scoring arising from the clarifications. The RFP stated the technical criteria would be evaluated independent of the cost portions of the bidder's proposals. The RFP also stated that, to the extent that there were no significant differences among the proposals, price would become increasingly significant. The ultimate purpose of the evaluation was to award a contract to the bidder whose proposal was the most advantageous to IEPA, cost and all other factors considered. Accordingly, the cost proposals were evaluated and weighed into the evaluation process at the completion of the technical evaluation.

Based upon the conclusions derived from the evaluation process described above, a contract was awarded to Roy F. Weston, Inc. of West Chester, PA. The requisite permit and approvals have been obtained and the remediation is proceeding on schedule.

REFERENCES

1. Illinois Environmental Protection Act, Section 39(h), Ill. Rev. Stat. 1985 Ch. 111½, para. 1039(h)

2. Frankel, I., N. Sanders and G. Vogel, March 1983, Survey of the Incinerator Manufacturing Industry, Chemical Engineering Progress, pp. 44-55.

3. Freestone, F. et. al., 1986, Evaluation of On-Site Incineration for Cleanup of Dioxin-Contaminated Materials, In: Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste. Proceedings of Twelfth Annual Research Symposium, EPA/600/9-86/022, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH., pp. 298-318.

4. Reed, J.C., S.R. Strauss and J.D. Cobb, 1986, Considerations in selecting a Transportable Thermal Destruction Unit (TTDU), In: Toxic and Hazardous Wastes. Proceedings of the Eighteenth Mid-Atlantic Industrial Waste Conference. G.D. Boardman (ed.), Technomic Publishing Co., Lancaster, PA., pp. 187-197.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

TRACING CONTAMINANT LEAKS USING BOREHOLE TELEVISION

Alan M. Jacobs
GEOPROBE
Pittsburgh, PA 15235, U.S.A.

ABSTRACT

Borehole television cameras are used to document stratigraphy or internal structure of wells, and can detect the presence and movement of fluids or solids. Cameras are designed for 2+-inch air- or water-filled boreholes. The images can be titled on the screen and videotaped with voice-dubbed notation. The tapes can be replayed for non-field personnel, permitting officials, and in courtrooms. Television has the advantage over other geophysical methods of downhole sensing in that one can actually see the features in question.

Contaminant leaks were investigated in 8 states. Monitoring wells had been placed at site perimeters to sample water-supply aquifers. The wells were installed with screens/slots at the aquifer horizons. Surface contamination from perched ground-water zones above the slots were sometimes caused by improper installation or damage to the well. Sometimes contaminants were observed entering the well through the slots at the horizon of the aquifer. Solids could be seen adhering to the casing, clogging the slots, settling in water, and oozing into the well at splices. Gasoline, having a different optical index of refraction from water, formed a visible layer floating on water.

Additional ground-water information in uncased boreholes has been collected by observing the water movement above and below the water level. The water could be seen entering or leaving the borehole where the hole intersects aquifers, fractures, and contacts between strata of different permeabilities. Quantitative measurements of flow could be obtained by duplicating the video image in the laboratory where a known flow-rate was produced.

INTRODUCTION

Television camera probes are presently being used to examine the subsurface strata, ground water, and the internal structure of well casings, screens, and down-hole instruments. This method allows actual real-time images to be monitored and recorded on videotape. The replay can be viewed immediately (no photo processing) or viewed later by others not involved with the field work, by permitting agencies, and in the courts.

Since 1980, the author has been asked to televise uncased boreholes and completed wells in Maryland, Tennessee, Louisiana, Pennsylvania, New Jersey, Nevada, Virginia, and California for the purpose of evaluating the hydrogeology of a site or to explain the movement of contaminants at hazardous-waste facilities and at cleanup sites. This paper summarizes what is being done using borehole television to detect and assess the movement of contaminants in ground water.

Preceding page blank

FEATURES OF BOREHOLE TELEVISION

The borehole television camera system used by GEOPROBE is manufactured by the Westinghouse Electric Corporation, Industrial and Government Tube Division, in Horseheads, New York. The camera can transmit a clear, high-resolution image to a surface TV monitor for the insitu inspection of subsurface conditions (1).

The closed-circuit TV system (ETV-1252) consists of a camera head (probe) and a camera control unit (CCU) connected by a flexible multilead underwater cable (Figure 1). The probe contains a 16-mm remote focus lens, a low-light level Newvicon pickup tube, quartz-halogen lighting on various attachments: down-hole viewer, side-hole viewer (with prism), combination down-hole wide-angle and side-hole viewer (with mirror), spotlight viewer (with prism), and directional spotlight (with prism and magnetic compass). The CCU contains remote focus and light-intensity controls. The cable contains armored, sheathed, and shielded bundles of single conductors (24) and coaxials (2), and is lowered and raised by an electric-powered cable reel and winch. This system is used with other video equipment for video-titling, tape recording, and monitoring. The down-hole portions of the system can operate under water and in a dry hole. The probe can be lowered and raised from air to water and from water to air without pausing. This ETV-1252 can survey wells as small as 50 mm in diameter and as deep as 150 meters.

In the field, a van functions as a mobile TV studio (Figure 2). The van protects the control, monitoring, and recording units from the elements. A sheave and boom guides the cable off the reel, out of the back of the van, and down the hole. Inside the van, the operator controls the descent/ascent, the focus and light intensity, the video recording, the audio-dubbing of verbal notation, and the video-titling using a character generator (depth, date, location, client, borehole number, hydro-geologic features, etc.). The amount of cable that is played out is noted by observing markings on the cable and entering depth values or elevation by means of a keyboard. Power (110 VAC) is provided by a gasoline-powered alternator.

Because the image is in black and white, the resolution is three-times better than with a similar color pickup tube. The ETV-1252 can televise a strand of wire only 1/3 the thickness of a human hair. It can focus from infinity down to the lens plate of the camera probe. The high resolution and closeup focus enables the camera to sit close to the object being televised; thereby allowing relatively clear images in murky water.

The probe is made of stainless steel, the down-hole attachments are made of either stainless steel or cast aluminum, and the cable sheath can be made of various flexible materials such as PVC, polyethylene, and polyurethane.

MONITORING-WELL INSPECTION

Monitoring During Drilling and Installation of Wells

During and after drilling, portions of the hole are either cased or uncased. In a cased hole the side-wall bedrock or soil cannot be viewed. The side walls can be televised prior to the installation of casing if the borehole can be kept open without casing. Well casing can be installed in stages with the upper part of the borehole cased to keep the side walls from caving and the lower part of the borehole uncased for televiewing.

The camera can be introduced into the hole during the drilling operation (between runs) if hollow-stem augers or wire-line methods are employed to look at the down-hole tools or peek out at the rock or soil in the bit area. The driller can usually guess about down-hole conditions, but seeing the situation first hand is more reliable. The driller can suggest the need for the camera during the drilling operation depending on the speed of drilling, bit resistance, loss of circulation of drilling fluids, tool drops, cuttings, etc.

The camera can also stand by during the installation of the casing and screens, the well development, and the grouting to see if materials are properly in place before proceeding to the next step. After completion of the installation, the well can be visually inspected by introducing the camera into the completed well.

Water Level

The measurement of the water level is usually accomplished by lowering a probe down the hole (Figure 3). The probe sends a signal to the surface when it touches the top of standing water. Discrete readings can be taken periodically in this manner. We have noticed that the probe can be triggered by moisture above the static water level, thus giving an erroneous reading. Perched water sometimes enters the casing through cracks or unsealed joints in the casing and sets off the probe. Droplets of water from condensation (not associated with ground water) can also trigger the probe. TV monitoring of the water table and comparison with the probing method should be done periodically.

If continuous readings are needed, a pulley can be installed which balances a float with a counterweight. The float rests on the water surface. If water levels change, the float and the counterweight adjust and the rotation of the pulley wheel moves a pen on a continuous recording chart. If unusual fluctuations are recorded, the camera should be used to visually check these fluctuations. One could perform a 1- or 2-day surveillance of the water table by videotaping the view of the top of the water column.

Water Sampling

Contaminants in the water column of a well are in solution or suspension. Dissolved material will come up with the water sample in a representative concentration. However, suspended material may not be present in the water sample in a representative concentration. Suspended solids (including oily residues) can stick to the sides of the casing, side wall, or slots and not come up with the water to be analyzed, thus being under-represented in the water sample. Suspended solids floating on the water or adhering to the sampling device can be over-represented in the water sample. Therefore, it is important to see the actual amount of suspended matter in the water column prior to sampling. The TV camera can be used to visually assess the actual amount of suspended solids in the well water at different depths (Figure 4).

Examining the Integrity of the Casing

A well with damaged casing may not fulfill its function of assessing the true ground-water conditions. In some cases, the well is used for detection of contaminants from a subsurface aquifer. For this, the well is installed so that the water entering the well comes only from the aquifer. This is accomplished by putting slots or screens only where the well intersects the aquifer. All other horizons are sealed (casing, grout, bentonite, etc.). If the casing is cracked (Figure 5) or if there is a leaky seal between joints of casing (Figure 4), however, the ground water from perched zones or from the surface can enter the well and contaminate the water. This may incorrectly indicate that the aquifer is contaminated.

Damaged casing can also provide incorrect water level data. If one wishes to measure the hydraulic gradient of a specific aquifer, the wells must be open only to the water of the specific aquifer. Cracks or holes in the casing may cause other strata (not being tested) to affect the level of the water in the well. The camera can locate damages in the casing.

Finally, if an obstructing object falls into the well, the camera can be used to determine what may be needed to remove the object.

Examining the Screens and Slots

The purpose of screens and slots, it to allow ground water to freely enter the well and prevent insitu sediment from coming in. The slots or screens actually keep back the gravel and/or sand in the annular space of the well that was installed to filter out the the soil and rock particles adjacent to the well. Proper well development using flushing techniques keeps the slots free of clogging matter. But how free are the slots? The camera can view the slots (Figure 6) and determine the effectiveness of the flushing.

While viewing the slots, one can see the movement of water and particulates. One can also see the stains made by contaminants. The specific gravity of the contaminant can be evaluated by seeing if its stain is above the slot (lighter than water) or below the slot (heavier than water). Sometimes one end of the suspended contaminant is sticking in the slot and the other end is waving in the flow of the water.

UNCASED BOREHOLES

Stratigraphic Analysis Prior to Installation of Monitoring Wells

Although the camera presently available to the author provides a black and white picture, the stratigraphy of subsurface strata can be evaluated in uncased holes. Rock type, bedding thickness, bedding features (cross-beds, graded bedding, presence of fossils), fractures (Figure 7) and voids can be identified. The presence of features that affect secondary permeability should be known prior to permeability testing.

Ground-water Movement

Above the static water level, a down-hole traverse with the TV camera probe will identify zones of perched water. Water flows into the hole in streams or droplets and then trickles or cascades down the hole. The water comes in, as would be expected, at fractures and at bedding-plane contacts, especially between formations of permeable and impermeable strata. Water sometimes comes in very slowly, a trickle or just moisture on the side hole. At other times the water comes in quickly in streams. One would expect the shape of the stream to be laminar or sheet like, because the fractures or planes that permit its entry are laminar and sheet like in form. However, the shape of the stream is usually pencil shaped (Figure 8); water virtually squirts into the hole. The direction of its spray is always towards the center of the borehole, no matter in what direction the regional ground water flows. The center of the borehole is the point of lowest pressure. There may be a section of borehole where one can see water flowing into the borehole from different and even opposite directions.

Below the water level one can identify movement of ground water in several ways. Water seldom will be turbulent. Normally the water movement is almost imperceptable. The movement can be observed by watching suspended-sediment particles moving in the flow of water. Flow caused by secondary permeability is easiest to see (Figure 9). A settling particle passing a fracture or bedding plane separation will be unaffected by it if there is no flow. The particle will be pushed away from the side wall if water is flowing into the hole. Or, the particle will be sucked in towards the side wall if water is flowing out of the hole. Flow into the borehole from the pore spaces of an aquifer is the most difficult to see; particles will be relatively more "active" than in non-aquifer zones.

QUANTITATIVE ANALYSIS

Contaminants in Suspension

Solids can be observed suspended in the ground water of a borehole or well. The actual identification must be done by sampling and laboratory analysis. As mentioned in a previous section of the paper, the specific gravity of the suspended material can be evaluated depending on whether it floats or sinks. The texture of the material would help to identify it. Some materials observed are fibrous (algal growth) or gelatinous (tar). Color television would help to further identify some of the materials.

Immiscible Liquid Contaminants

One of the wells examined by the author was tested for the amount of gasoline contamination. Gasoline floats on water and has a different index of refraction from water. The camera probe was lowered into the fluid column. It passed into one liquid and then into another. A clearly defined miniscus was present and easily seen between the upper (gasoline) and lower (water) fluid layers. The volume of gasoline was calculated by using the value measured by the television probe of the thickness of the gasoline layer.

Measuring Flow Rates

To quantify flow rates, one should recreate the visual image in a laboratory with the sizes to proper scale. The TV camera can be used in the laboratory to verify the image. The flow or discharge rates of perched water and saturated-zone water can be measured in this fashion.

Recovery of the water level during down-hole pump tests, could also be observed with the camera. One could also evaluate the effect of perched water zones on the recovery rate of the water level.

CONCLUSIONS

The use of borehole television for the detection and assessment of the contamination of ground water is an important breakthrough in the technology available to the hazardous-waste management industry. Current technology provides a black and white, high-resolution image from equipment that can be used in most underground situations. The addition of color-television borehole probes, presently being introduced, will make this technique more valuable to this industry.

REFERENCES

1. Beyer, R. R., and A. M. Jacobs, 1986, Borehole TV for the Problem Sites...A New Investigative Tool, Engineering and Mining Journal, May 1986.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

FIGURE 1 - Borehole Camera with Lighted Attachments.

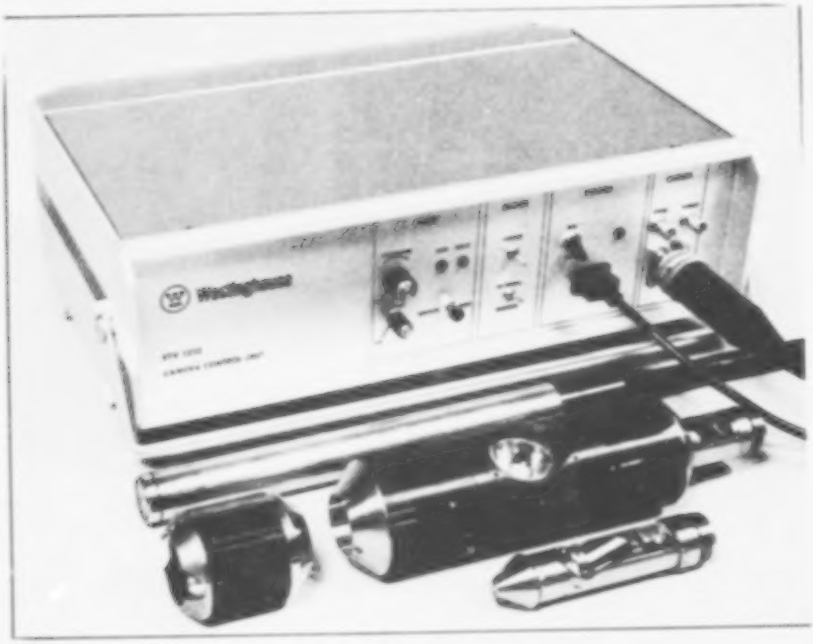

Westinghouse

FIGURE 2 - TV Van

FIGURE 3 - Down-hole View of Surface of Static Water Level.

FIGURE 4 - Suspended Solids Leaking into Well and Adhering to the Casing.

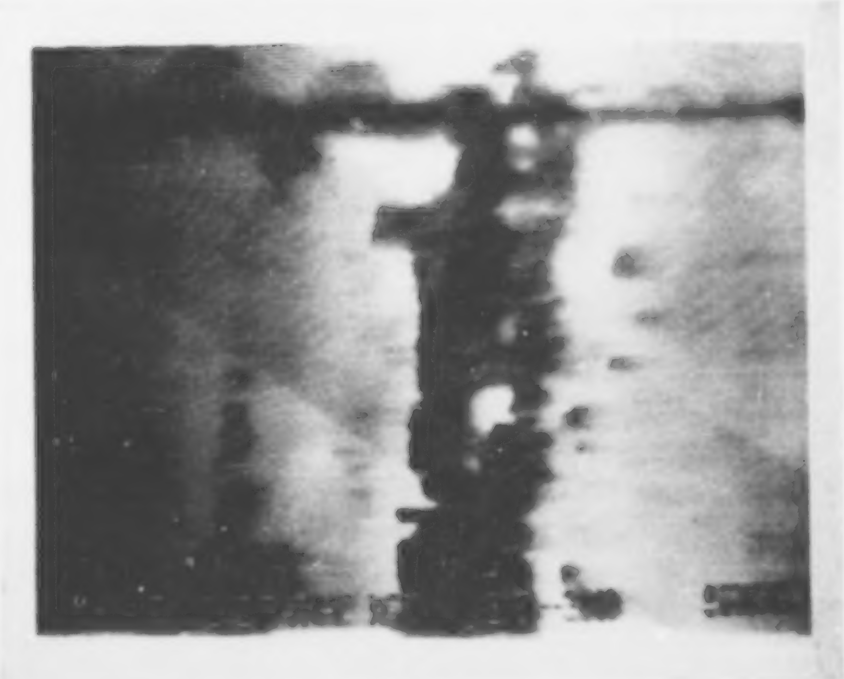


FIGURE 5 - Cracked Casing and Grouted Annular Space

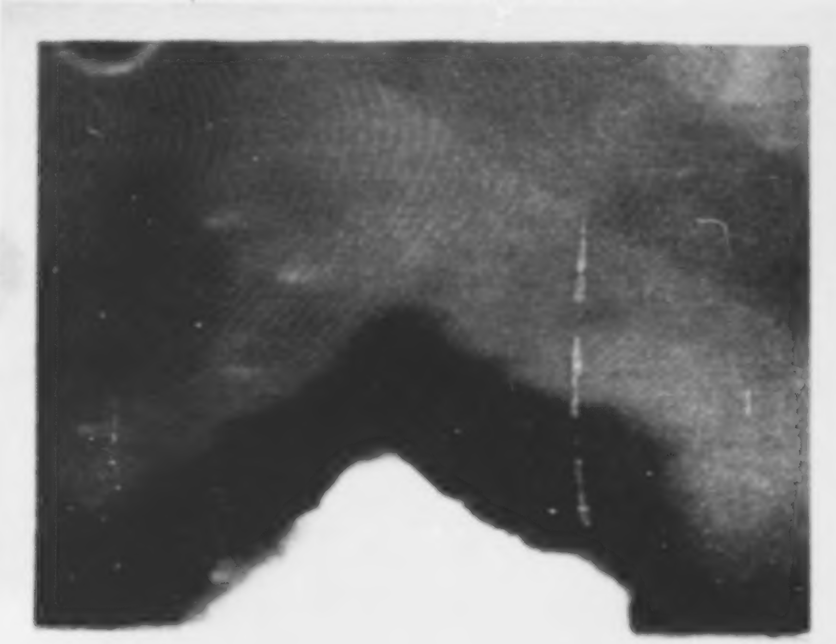


FIGURE 6 - Slotted Casing (Underwater) as Seen in Elliptical Mirror at Upper Right.

FIGURE 7 - Horizontal Fracture in Bedrock

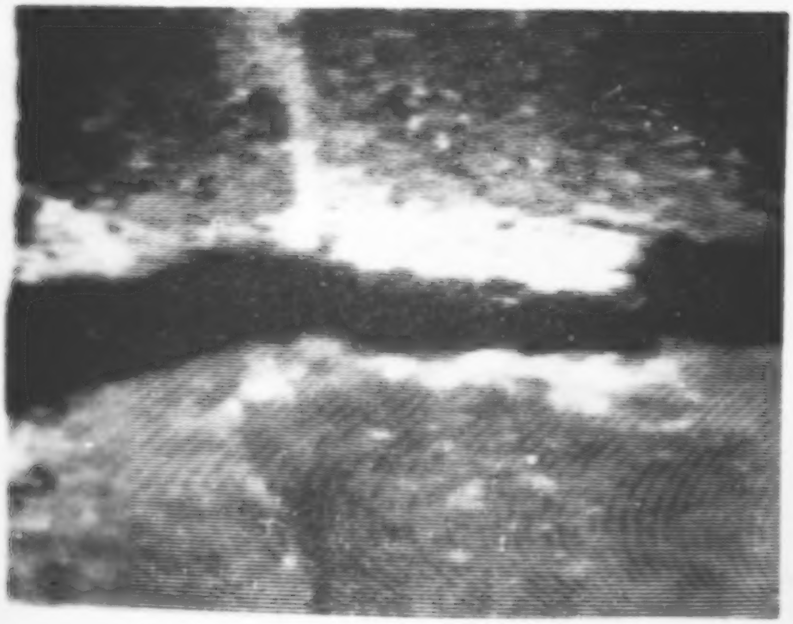


FIGURE 8 - Pencil-shaped Streams of Water from Perched Aquifer

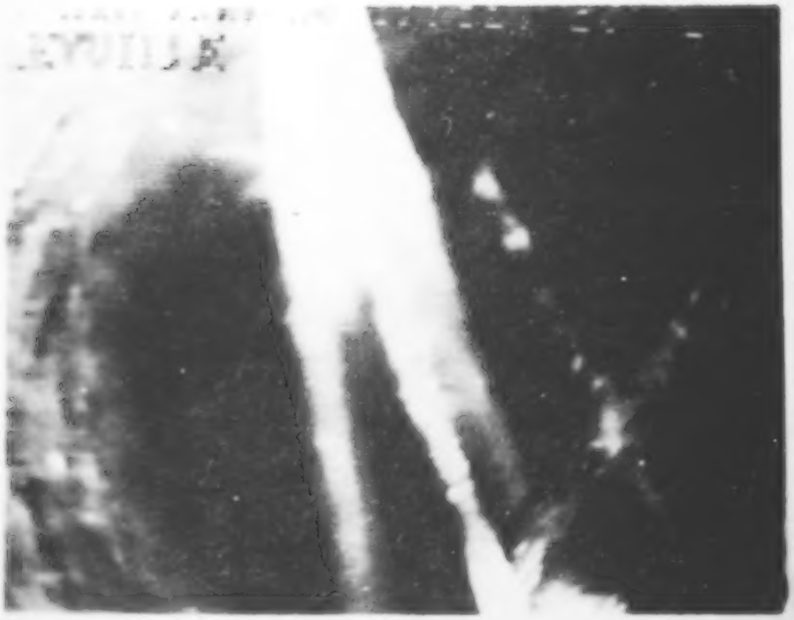


FIGURE 9 - Sediment Moving in Flow of Water from Fracture at 323-ft Depth

THE EFFECT OF pH ON 2,4-D BIODEGRADATION

G. L. Sinton, L. E. Erickson and L. T. Fan
Department of Chemical Engineering
Durland Hall
Kansas State University
Manhattan, Kansas 66506

ABSTRACT

Considerable uncertainty exists as to if and how 2,4-dichlorophenoxyacetic acid (2,4-D) inhibits microbial growth. The uncertainty may be induced totally or partially by the observed inhibition effects of a metabolic product 2,4-dichlorophenol (2,4-DCP). The results of experiments with Pseudomonas sp. NCIB 9340 in one and two liter fermenters have shown that culture pH is an important factor in determining the growth rate of this microorganism and the extent of 2,4-DCP accumulation. Experiments with 1-liter batch fermenters over a pH range of 5.1 to 9.4 have shown that the highest growth rates occur between pH 6.5 and 7.9; the specific growth rate decreases as the pH is increased or decreased from this range until it reaches zero at 9.4 or 5.1 respectively.

Extensive accumulation of 2,4-DCP occurred at a low pH; it was accompanied by a reduction in the biodegradation rate, presumably due to inhibitory effects of 2,4-DCP. 2,4-D biodegradation ceased completely when the concentration of 2,4-DCP reached about 44 mg/L. No growth was observed even after the 2,4-DCP concentration was reduced by non-biodegradation mechanisms and new 2,4-D substrate was subsequently added to the culture. Cultures exhibiting no growth for seven days at pH 5.1 could be revived to resume normal growth by increasing the pH to 6.0.

INTRODUCTION

2,4-Dichlorophenoxyacetic acid (2,4-D) is an aquatic and terrestrial herbicide. It has been selected as a model compound for study because of its wide use and structural similarity to other toxic and hazardous compounds currently of interest, such as other halogenated aromatic and phenolic compounds. Furthermore, 2,4-D is among 38 compounds that the EPA has proposed to add to a list of chemicals used for identifying wastes as hazardous and appropriate for management under the Resource Conservation and Recovery Act (19).

Organisms capable of degrading 2,4-D were studied in pure and mixed cultures mostly under aerobic conditions (20). A typical metabolic pathway is illustrated in Fig. 1 (4). Numerous investigations were undertaken to develop kinetic models for the biodegradation of 2,4-D and

Preceding page blank

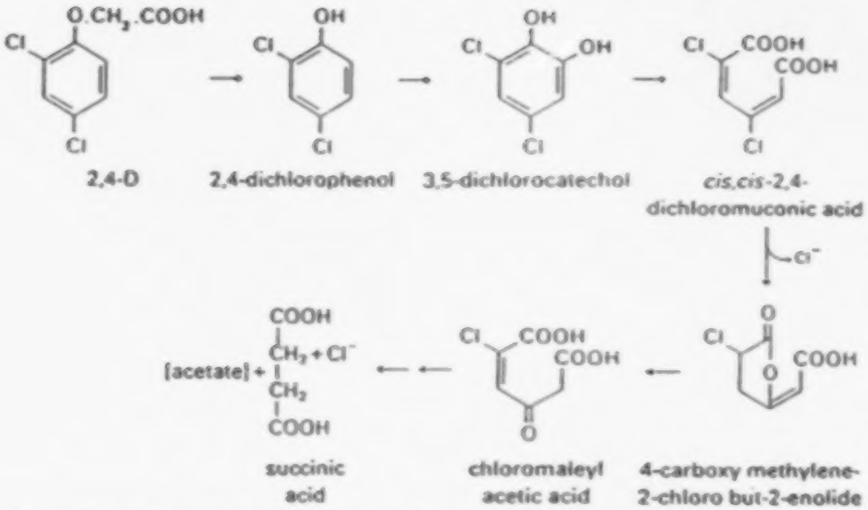

O.CH₂.COOH
Cl
Cl
2,4-D
OH
2,4-dichlorophenol
OH
OH
3,5-dichlorocatechol
COOH
COOH
cis,cis-2,4-dichloromuconic acid
Cl⁻
O
COOH
4-carboxy methylene-2-chloro but-2-enolide
COOH
COOH
O
chloromaleyl acetic acid
COOH
CH₂ + Cl⁻
[acetate] +
CH₂
COOH
succinic acid

Figure 1. Aerobic pathway for 2,4-D biodegradation (Cripps, R. E., and Roberts, T. R.) (4).

related compounds (2,10,14-17,22). These studies have given rise to various models, some of which appear to yield conflicting results. Part of the diversity among these models can be attributed to the variability of experimental conditions, such as pH, temperature, aeration, supplemental nutrients, culture enrichment, and substrate concentration range, all of which have been found to affect appreciably the rates of biodegradation (20).

Many of the proposed biodegradation models do not account for inhibition effects (2,10,16,22). Most of them are of the Monod type:

$$\mu = \mu_{max}[S]/(K_s + [S]) \qquad (1)$$

Specifically, e.g., Tyler and Finn (22) have reported that this model accurately describes growth on 2,4-D up to 2000 mg/L and for 2,4-DCP up to 25 mg/L. Moreover, they have found that 2,4-DCP inhibits growth at concentrations above 25 mg/L.

Considerable uncertainty exists as to if and how 2,4-D itself is actually inhibitory. Some researchers have reported inhibitory effects of 2,4-D at various levels such as 35 mg/L and 45 μg/g-soil (14,17). Others (2,10,16,22) have successfully employed versions of the Monod model that neglect inhibitory effects. The uncertainty may be induced totally or partially by the observed inhibition effects of a metabolic product, e.g., 2,4-DCP. Several researchers have found 2,4-DCP to be inhibitory at relatively low concentrations (3,12,22)

The Haldane model

$$\mu = (\mu_{max}[S])/([S] + K_s + ([S]^2/K_I)) \qquad (2)$$

appears to be the most promising model for the description of inhibitory substrate degradation. Numerous researchers have successfully fitted this model to their degradation data for 2,4-D or related compounds such as phenols or benzoate (6,14,18,21); nevertheless, it does not appear to fit the data of Tyler and Finn (22) well.

PURPOSE

The primary goal of this research is to examine the effects of pH on the rate of 2,4-D biodegradation. The forms of 2,4-D biodegradation models and the values of their kinetic parameters need be clarified to understand the mechanism of 2,4-D biodegradation under a variety of conditions. An understanding of the effects of pH is essential for the design and evaluation of biological treatment options to eliminate production wastes and to manage biodegradation in field applications. The pH should also be considered in assessing environmental persistance of 2,4-D and in determining if undesirable metabolic products are produced as a result of 2,4-D biodegradation.

APPROACH

Organism and Media

The organism used in the present experiments was Pseudomonas sp. NCIB 9340. The growth media for this organism contained the following: 1.5 g/L of K_2HPO_4; 0.2 g/L of $MgSO_4 \cdot 7H_2O$; 0.05 g/L of $CaSO_4 \cdot 2H_2O$; 0.5 g/L of NH_4NO_3; 0.5 mg/L of $FeSO_4 \cdot 7H_2O$; de-ionized water; and either 2,4-D or 2,4-DCP as the sole source of carbon. Cultures of the organism were continuously maintained to provide inocula throughout the experiments by regular subculturing in shake flasks with either 2,4-D or 2,4-DCP as the carbon source. The pH and temperature of the maintenance cultures were not controlled but generally remained at levels of 6.5 to 6.9 and 22 to 25°C, respectively.

Assays

Substrate and product concentrations were assayed by high performance liquid chromatography (HPLC); a Varian MCH-10 column was employed (monometric octadecasilane bonded to silica). Detection was accomplished by UV absorption at 283 nm. Acetonitrile and 0.015 N H_2SO_4 served as solvents in a gradient elution. This HPLC procedure made it possible to analyze aqueous samples directly without any extraction or concentration. The only sample preparation required was filtration through a 0.45 µm nitrocellulose filter to remove the biomass. Biomass concentration was monitored using a Bausch and Lomb Spectronic 20 to measure absorbance at 545 nm.

Batch Fermentations

Batch fermentations were conducted in one and two liter fermenters by controlling pH, temperature, aeration, and stirring rate (temperature = 25°C, aeration = 0.65 vvm, stirring rate = 700 rpm). These controlled variables as well as the concentrations of biomass, 2,4-D and 2,4-DCP were monitored. Experiments were conducted over a pH range between 5.1 and 9.4; the initial concentration of 2,4-D was 200 mg/L.

PROBLEMS ENCOUNTERED

The determination of an appropriate method of storage for Pseudomonas sp. NCIB 9340 to provide a consistent source of inocula was the major difficulty encountered in the present research. It has been known that biodegradation rates of 2,4-D and other xenobiotic compounds can be greatly increased by allowing the organisms responsible for the degradation to become acclimated to the new substrates (1,10,13). Thus, it is desirable to have experiments inoculated with organisms that are equally acclimated to the test substrate. In an attempt to provide a supply of organisms with a uniform history of acclimation, the original freeze-dried sample of Pseudomanas sp. NCIB 9340 was revived and grown on 2,4-D. It was then dispensed into a large number of test tubes containing the regular 2,4-D media, as listed in the approach, plus 10 weight percent glycerol. Subsequently, these samples were placed in a freezer at -10°C for long-term storage. Unfortunately this method of storage caused the organism to loose its ability to degrade 2,4-D and 2,4-DCP. Storage on refrigerated agar slants was also attempted; however, revival of 2,4-D degrading organisms was generally not possible after more than about two weeks and was very inconsistent even over shorter intervals.

The genes required for the biodegradation of xenobiotic materials are often found on plasmids (5,7-9). Based on the assumption that the ability of Pseudomonas sp. NCIB 9340 to degrade 2,4-D was plasmid mediated, Leslie (11) at the National Collections of Industrial and Marine Bacteria Ltd. investigated several storage methods in response to our inquiries concerning long term storage of the organism. Pseudomonas sp. NCIB 9340 plasmid DNA was well maintained by regular subculturing on 2,4-D, and storage in liquid nitrogen apparently maintained the plasmids, but at a somewhat lower level. Finally, in agreement with our results, storage in 50% glycerol at -20°C is unsuitable for plasmid maintenance.

Because of the failure of the glycerol and the agar slant methods, regular subculturing was selected as the procedure for culture maintenance. It is generally observed that after a certain period of acclimation the organisms are not greatly affected by further acclimation (10); thus this method should provide fairly consistent inocula.

RESULTS

The shake flask experiments gave no indication of substrate inhibition by 2,4-D in the concentration range from 0.0 to 370 mg/L. In the 50.4, 94.5, 198, and 370 mg/L shake flask experiments, accumulation of 2,4-DCP was observed to reach levels of 0.1, 1.0, 13.2, and 16.9 mg/L, respectively. The 2,4-DCP and 2,4-D were eventually completely degraded. The data from the flask initially containing 2,4-D at 198 mg/L in Fig. 2 illustrate the basic pattern of the substrate and product concentration profiles obtained in the shake flask experiments. The pH in these experiments were not controlled; it generally dropped from the initial value of 6.8 to about 6.4 to 6.7 with the largest drop occurring in the flasks with the highest initial concentration of 2,4-D.

The results of experiments in 1-liter batch fermenters with 2,4-D as the substrate indicate that culture pH is a significant factor in determining growth rates. Figure 3 demonstrates the relation between the pH and specific growth rate. The latter was obtained from the slope of a logarithmic plot of the biomass concentration against time during the exponential growth phase. The highest specific growth rates were observed in the pH range from 6.5 to 7.9. The specific growth rate decreased as the pH was increased up to 9.4 where no growth or biodegradation was observed over a period of four days. The specific growth rate also decreased as the pH was reduced from 7.0 to 5.1; at pH 5.1, no growth

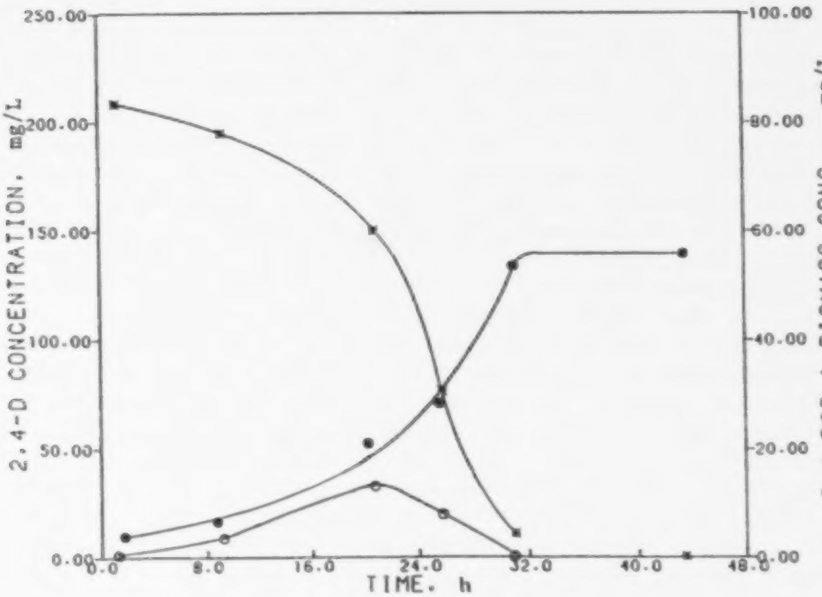


Figure 2. 2,4-D degradation by Pseudomonas sp. NCIB 9340 in a shake flask at 25 C and initial pH = 6.8; ● , biomass concentration; * , 2,4-D concentration; o , 2,4-DCP concentration.

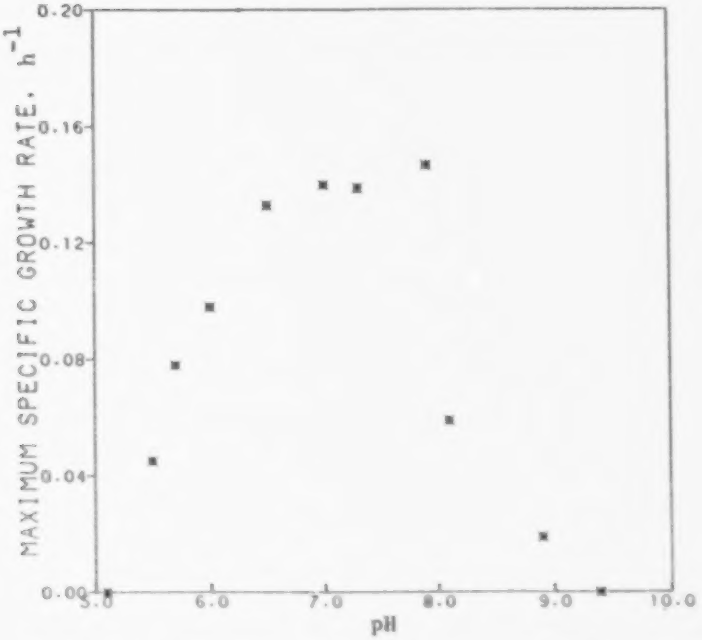


Figure 3. Effect of pH on the maximum specific growth rate of Pseudomonas sp. NCIB 9340 growing on 2,4-D in batch fermenters at 25 C.

was observed. Cultures exhibiting no growth for seven days at pH 5.1 could be revived to resume normal growth and substrate consumption by increasing the pH to 6.0.

Appreciable accumulation of 2,4-DCP was observed in batch fermentation experiments conducted at pH 5.5 and 5.7. These were the two lowest pH levels where growth was observed. In both cases the accumulation of 2,4-DCP appears to have completely stopped the biodegradation of 2,4-D. In the pH 5.7 experiment, the 2,4-DCP concentration reached 49.5 mg/L with 2,4-D biodegradation stopping at 38 mg/L. No further growth or degradation was observed even after the 2,4-DCP concentration was decreased to below 20 mg/L and additional 2,4-D substrate was supplied. The pH 5.5 experiment resulted in 2,4-DCP accumulating to 44.5 mg/L with 2,4-D biodegradation stopping at 84 mg/L as shown in Fig. 4. The specific growth rates given in Fig. 3 for pH 5.5 and 5.7 were based on growth before significant amounts of 2,4-DCP accumulated. Accumulation of 2,4-DCP is accompanied by a reduction in the biodegradation rate, presumably due to inhibitory effects of 2,4-DCP. The results of experiments in 2-liter batch fermenters with 2,4-DCP as the only carbon source have indicated a strong inhibitory effect above concentrations of 30 to 35 mg/L.

2,4-DCP accumulation does not appear to be a factor in reduction of the growth rate in the higher range of pH (above pH 7), but it affects appreciably the growth rate in the low pH range where it can inhibit and possibly completely arrest the degradation of 2,4-D. It is not clear why 2,4-DCP accumulation was observed at slightly higher values of pH in the shake flasks; this may be due to a difference in vapor loss or other nonbiodegration mechanisms compared to that observed in the fermenters.

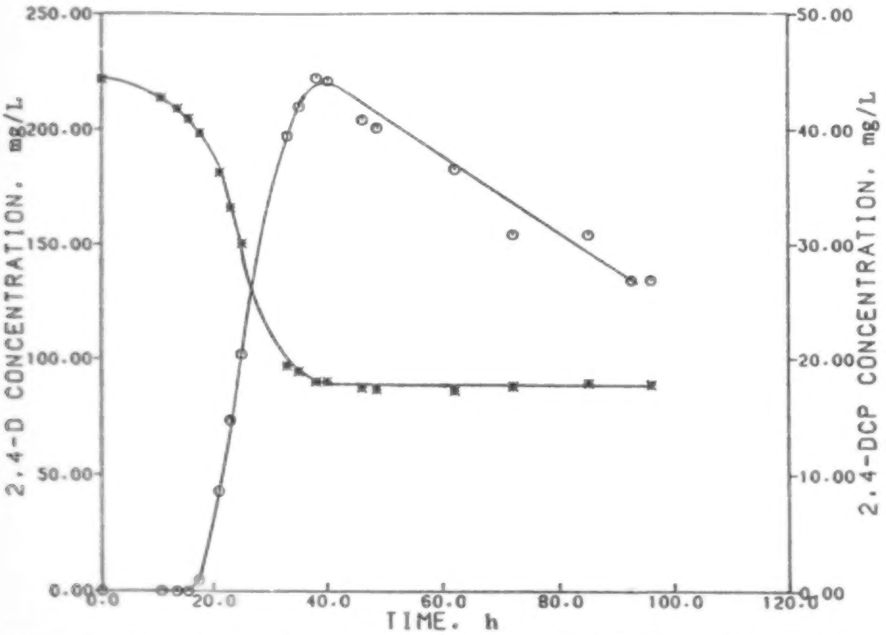


Figure 4. 2,4-D degradation by *Pseudomonas* sp. NCIB 9340 in a 1-liter batch fermenter at pH 5.5 and 25 C; * , 2,4-D concentration; o , 2,4-DCP concentration.

CONCLUSIONS

The shake flask and batch fermentation experiments gave no indication of inhibition of growth by 2,4-D. Accumulation of 2,4-DCP was observed in the shake flask experiments but all of the 2,4-D and 2,4-DCP were completely eliminated eventually. The Batch experiments with 2,4-D indicated that pH is an important factor in determining growth rates. The highest growth rates were observed between pH 6.5 and 7.9. Accumulation of 2,4-DCP was also dependent on pH; accumulation occurred at pH 5.5 and 5.7, the lowest pH levels where growth was observed. In these two cases, the accumulation of 2,4-DCP appears to have stopped the biodegradation of 2,4-D, possibly killing the microbial population. 2,4-DCP inhibits growth above concentrations of about 30 mg/L.

ACKNOWLEDGEMENT

This work was conducted under the sponsorship of the Engineering Experiment Station (Office of Hazardous Waste Research) of Kansas State University.

1. Audus, L.J., 1964, Herbicide Behavior in the Soil, In: The Physiology and Biochemistry of Herbicides, Academic Press, New York, pp. 163-189.

2. Banerjee, S., Howard, P.H., Rosenberg, A.M., Dombrowski, A.E., Sikka, H. and Tullis, D.L., 1984, Development of a General Kinetic Model for Biodegradation and its Application to Chlorophenols, Environ. Sci. Technol., Vol. 18, pp. 416-422.

3. Beltrame, P., Beltrame, P.L., and Carniti, P., 1984, Kinetics of Phenol Degradation by Activated Sludge in CSTR, Chemosphere, Vol. 13, pp. 3-9.

4. Cripps, R.E., and Roberts, T.R., 1978, Microbial Degradation of Herbicides, In: Pesticide Microbiology, (Hill, I.R., and Wright, S.L.J. eds.) Academic Press, New York, pp. 670-677.

5. Don, R.H., and Pemberton, J.M., 1981, Properties of Six Pesticide Degradation Plasmids Isolated from Alcaligenes paradoxus and Alcaligens eutrophus, J. Bacteriology, Vol. 145, pp. 681-686.

6. Edwards, V.H., 1970, The Influence of High Substrate Concentrations on Microbial Kinetics, Biotechnol. Bioeng., Vol. 12, pp. 679-712.

7. Fisher, P.R, Appleton, J., and Pemberton, J.M., 1978, Isolation and Characterization of the Pesticide-Degrading Plasmid pJP1 from Alcaligenes paradoux, J. Bacteriol., Vol. 135, pp. 798-804.

8. Friedrich, B., Meyer, M., and Schlegel, H.G., 1983, Transfer and Expression of the Herbicide-degrading Plasmid pJP4 in Aerobic Authtrophic Bacteria, Arch. Microbil., Vol. 134, pp. 92-97.

9. Ghosal, D., You, I.-S., Chatterjee, D.K. and Chakrabarty, A.M, 1985, Microbial Degradation of Halogenated Compounds, Science, Vol. 228, pp. 135-142.

10. Hemmett, R. and Faust, S., 1969, Biodegradation Kinetics of 2,4-D

by Aquatic Microbes, Res. Review, Vol. 29, pp. 191-206.

11. Leslie, C.E., 1986, private communication, December 4, 1986.

12. Liu, D., Thomson, K., and Kaiser, K.L.E., 1982, Quantitative Structure-Toxicity Relationship of Halogenated Phenols on Bacteria, Bull. Environ. Contam. Toxicol., Vol. 29, pp. 130-136.

13. Loos, M.A., 1975, Phenoxyalkanoic Acids, In: Herbicides: Chemistry, Degradation and Mode of action, (Kearney, P.C., and Kaufamn, D.D., eds.) 2nd Ed., Marcel Dekker Inc., New York, Vol. 1, pp. 1-56.

14. Papanastasiou, A.C., and Maier, W.J., 1982, Kinetics of Biodegradation of 2,4-Dichlorophenoxyacetate in the Presence of Glucose, Biotechnol. Bioeng., Vol. 24, pp. 2001-2011.

15. Paris, D.F., Lewis, D.L., Barnett, J.T., Jr., and Baughman, G., 1975, Microbial Degradation and Accumulation of Pesticides in Aquatic Systems, EPA-660/3-75-007, Southeast Environmental Research Laboratory, National Environmental Research Center, U.S. EPA, Athens, Georgia, 30601.

16. Paris, D. F. Steen, W.C., Baughman, G.L. and Barnett, J.T., Jr., 1981, Second-Order Model to Predict Microbial Degradation of Ogranic Compounds in Natural Waters, Appl. Environ. Microbiol., Vol. 41, pp. 603-609.

17. Parker, L.W., and Doxtater, K.G., 1982, Kinetics of Microbial Decomposition of 2,4-D in Soil: Effects of Herbicide Concentration, J. Environ. Qual., Vol. 11, pp. 679-689.

18. Pawlowsky, U., and Howell, J.A., 1973, Mixed Culture Biooxidation of Phenol. I. Determination of Kinetic Parameters, Biotechnol. Bioeng., Vol. 15, pp. 889-896.

19. Rich, L.A., 1986, EPA Broadens its List of Hazards, Chemical Week, Vol. 139, July 2, pp. 26-27.

20. Sinton, G.L., Fan, L.T., Erickson, L.E. and Lee, S.M., 1986, Biodegradation of 2,4-D and Related Xenobiotic Compounds, Enzyme Microb. Technol., Vol. 8, pp. 395-403.

21. Sokol, W., and Howell, J. A., 1981, Kinetics of Phenol Oxidation by Washed Cells, Biotechnol. Bioeng., Vol. 23, pp. 2039-2049.

22. Tyler, J.E., and Finn, R.K., 1974, Growth Rates of a Pseudomonad on 2,4-D and 2,4-Dichlorophenol, Appl. Microbiol., Vol. 28, pp. 181-184.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

INDEX

acid
  wastes, 33
  neutralization capacity, 34
acrylates, 23
Africa
  mining wastes, 21
air
  sampling of, 12
air stripping, 42
ash
  incinerator, 18
  residual, 3
assays
  pH-stat, 23
ASW matrix
  concentrated, 20
attenuation, 33
Atterberg limits, 45
audits
  waste minimization, 59
Australia
  mining wastes, 21
bacterial
  treatment, 26
barium, 57
Batch Reactor, 15
bentonite, 15
bioaccumulation, 50
bioassays
  jet fuel contamination, 14
  plant responses to petrochemical wastes, 24
biodegradation, 39
  in-situ, 25
  lignin, 28
  microbial, 14
  of 2,4-D, 62
  P. chrysosporium, 28
  soil, 13
  white rot fungus, 28
biological
  treatment, 41
biphenyls, 28
boilers
  industrial, 1
  watertube, 21
BS procedure
  penetrometry testing, 33
buffers
  borate, 23
calcium
  alginate, 23
  silicate matrix, 33
  sulfate, 56

Cambridge-Stereoscan, 57
Canada
  mining wastes, 21
carbon
  activated, 17
carbon dioxide
  evolution, 14
carbonyl diimidazole, 23
Carl Zeiss-Jena TUR M-62, 57
cell
  lined, 16
cement, 30
chemical
  destruction, 43
China
  electroplating wastes, 55
  mining wastes, 21
chloride
  acryloyl, 23
chlorine
  contamination, 6
  destruction, 43
  organo- compounds, 30
chromium
  removal of, 8
  waste recovery/reuse, 55
clay
  soil liners, 47
cleaning system
  flue gas, 23
closure
  cost, 52
coal
  conversion residuals, 27
combustor
  secondary, 6
compressive strength, 33, 34
conductivity
  hydraulic, 33, 34
contamination
  groundwater, 11
  hydrocarbon, 11, 14
  soil, 11, 14
Cracov, Poland, 11
creosote, 13
cultivars, 39
cutoff walls
  plastic/concrete, 19
cyanide
  destruction of, 41
  waste, 33
  oxidation of, 9
Daphnia, 13, 39

decontamination
  electrical equipment, 36
  Polychlorinated biphenyls (PCBs), 36
  soil, 7
  transformers, 36
degradation
  oily wastes, 50
  proteolytic, 23
density
  bulk, 12
Department of the Environment (DOE), UK, 18
desorption
  thermal, 4
destruction
  chemical, 43
  cyanide, 41
  thermal, 31, 37, 39
Destruction Removal Efficiency (DRE), 1, 2
Detoxifier System, 54
dioxins
  waste incineration, 39
  chlorinated, 43
disposal
  of solid hazardous waste, 29
distillation
  batch, 59
  leachate, 38
  process of, 41
  solvent, 9
drainage front, 20
dust
  clay or kiln, 30
  filter, 35
  lime, 30
economics
  evaluation, 58
electrical equipment, 36
electrodes, 8
electronic capacitor
  manufacture of, 59
electroplating plants, 55
  sludges from, 55
electrostatic precipitator, 30
electro-kinetics
  DC electrical field, 8
encapsulation
  micro-, 23
  surface, 33
entrapment, 33
  gel, 23
enzymes
  chymotrypsin; covalent attachment of;
  crosslinking of; crystalline;
  stabilization of, 23

evaluation
  capital project, 58
evaporation
  process of, 38
extraction
  equilibrium, 34
  method of, 7
  PCDD/PCDF, 43
  sequential chemical, 34
  treatment, 7
Federal Republic of Germany
  mining wastes, 21
ferrous
  phosphates, 56
fire hazards, 11
fixation (see solidification)
  metal, 30
  soluble silicates, 30
flexible membrane liners (FMLs)
  polyethylene, 47
flow rates
  distribution in field soils, 22
flue gas
  samples, 1
flyash, 30, 37
  samples, 1
solidification, 33
furans
  chlorinated, 43
Furnace Bottom Ashes (FBAs), 18
gas
  odours, 18
gasoline
  contamination, 61
gel
  stabilization, 30
glacial drift deposit, 11
glutaraldehyde, 23
grasses
  bent-; brome-; dessication of;
  reed canary-, 39
gravity
  of specific solids, 12
groundwater
  contamination, 11, 14
  movement, 61
grouting
  injection, 30
Harwell, Waste Research Unit, UK, 33
hazardous wastes
  management of, 12
  treatment of, 9, 32
heat
  recovery, 10

homogenization
  tissues of, 23
hydraulic
  conductivity, 33, 34, 45
  measures, 25
hydrocarbons
  contamination, 11
  aromatic, 25
  polynuclear aromatics, 27
  in-situ treatment of, 54
hysteresis, 20
immobilization
  degradation, 50
incineration, 3
  dioxin waste, 39
  hazardous waste, 35
  mobile system, 60
  oily sludge, 16
  Polychlorinated Biphenyls (PCBs),
  rotary kiln, 16
  slag, 5
incinerator
  liquid, 6
  MWP-2000, 6
industrial wastes
  disposal, 53
inorganic
  acid wastes, 33
  wastes, 33
irrigation (water), 30
jet fuel
  contamination, 14
Kuwait, Shuaiba Industrial Area (SIA), 16
land treatment
  oily wastes, 50
landfarm facilities, 16, 39
landfills, 51
  central low point, 52
  design/operation, 52
  gas odours, 18
  hazardous wastes, 38
leachate test
  dynamic, 34
leachates, 27
  collection, 42
  distillation, 38
  reduction, 52
  monitoring of, 46
  organic halides, 46
  synthesis of clay, 47
  Total Organic Carbon (TOC), 46
  treatment of, 15

leaching, 3
  characteristics of, 33
  hydraulic, 8
leaks
  identification, 52
  contaminant, 61
least cost alternative, 23
liners
  clay, 47
  Flexible Membrane Liners (FMLs), 47, 52
link system, 57
Low-Level Wastes (LLW)
  treatment of, 32
management
  hazardous waste, 12
matrix
hydrated calcium silicate, 33
membranes
  high pressure, 48
  latex, 45
  swelling tests, 45
metals
  bearing slags, 33
  emission, 37
  finishing industries, 33
  hydrated ions, 30
  polyvalent, 30
  solidification, 30
microbiology, 25
microtox test, 46
  biodegradation, 13
migration
  ionic, 8
minimization
  wastes, 59
mining wastes
  Africa; Australia; Canada;
  China; Federal Republic of Germany;
  legislation; Poland; research;
  United Kingdom; USSR, 21
MODAR oxidation process, 10
nerve gas, 12
neutralization
  of caustic/acid wastes, 33
new housing land, 51

Oak Ridge National Laboratory (ORNL), 32
oedometer, 8
Oily Waste Extraction Procedure (OWEP), 30
organics, 40
  free-phase, 20
  gross (disappearance of), 15
  particulate/semi-volatile, 1
  polymer, 33
  refractory, 15

outflow
  clay soils, 22
oxidation
  cyanide, 9
  thermal, 58
oxygen
  demand, 27
  rate of uptake, 27
PCDD/PCDF, 43
penetrometry testing
  BS procedure, 33
pesticides, 23
petrochemical
  phytotoxicity, 39
  wastes, 39, 24
pH
  effects on 2, 4-D, 62
phase interactions
  mass transfer, 20
phosphate
  ferrous, 56
Photobacterium phosphoratum, 46
phytotoxicity
  petrochemical, 39
pigments
  oxide, 56
pilot scale, 41
plastic
  slurry walls, 19
Poland
  mining wastes, 21
  remedial action, 11
pollutants
  enhanced movement of, 8
Polychlorinated Biphenyls (PCBs)
  contamination of, 6, 26
  decontamination of, 36
  metabolism of, 26
polymerization (co-), 23
Polytetrafluoroethylene (PTFE), 18
Portland Cement, 33
post-closure, 52
Powdered Activated Carbon Treatment (PACT), 17
pozzolanic processes, 33
precipitation, 41
Principle Organic Hazardous Constituent, (POHC) 1, 2
prototype test
  hydrocarbon treatment, 54
Pseudomonas
  biodegradation, 62

Pulverised Fuel Ash (PFA), 18
pyrolysis
  plasma arc, 2
quality prediction
  solidification process, 33
Q-150 OD Paulik-Erdey derivatograph, 57
radioactive
  wastes, 12
Radioactive Mixed Wastes (RMW)
  treatment of, 32
reactor
  squelching batch, 27
recovery
  heat, 10
  secondary solvent, 58
  waste chromium of, 55
recycling, 59
reduction
  source, 58
remedial action
  hydrocarbon contamination, 11
remediation
  soil, 27
retarders, 30
reuse
  waste chromium of, 55
robotic technology, 12
rotary kiln
  incineration, 4
Rotating Biological Contactor (RBC), 15
Royal Arsenal
  Woolwich, London, 51
Saint Vulbas, France
  incinerator plant, 36
salt caverns
  hazardous waste disposal, 29
  repository, 29,53
salts
  hardening, 57
scrubbing system
  exhaust gas, 30
Shuaiba Industrial Area (SIA), Kuwait, 30
silicates
  fixation of, 30
slags, 35
  extraction, 5
  incineration, 5
  metal-bearing, 33
sludges, 30
  alkylation, 39
  and lime dust, 30
  electroplating waste, 55
  farming of, 30
  homogenous, 30

  Kuwait, 16
  oily, 16
  supercritical fluid, 40
slurries, 30
  filter presses, 48
  walls, 48
slurry wall
  durability of, 45
sodium hydroxide, 33
sodium hypochlorite, 33
soils
  catalytic oxidation, 40
  clay, 22
  contamination of, 11, 14, 26, 31
  decontamination, 7
  fluid extraction, 40
  humus content, 30
  remediation of, 27
solidification techniques
  silicate-based, 33
  site-specific, 33
solidification technology, 33
  cement-based;
  hazardous wastes;
  inorganic wastes;
  long-term stability;
  quality control
solids (dry), 9
solvents, 59
  distillation of, 59
stabilization
  gel, 30
steam stripping
  process of, 41
stillbottom
  trichlorophenol, 39
sulfates
  calcium, 56
supercritical fluids
  extraction of, 44
Superfund sites, 8
  Stringfellow,15
  New Lyme, 15
supernatant production, 33
television
  borehole, 61
Test & Evaluation Facility (T&E), 15
tests
  freeze/thaw, 34
  wet/dry, 34
Thames Barrier
  London Flood Prevention, 51
Thamesmead, London, UK, 51

thermal
  desorption, 4
  destruction, 37, 39
  oxidation, 58
  vitrification, 31
thermoplastic processes, 33
toxicity test, 46
Toxicity Char. Leaching Proc. (TCLP), 9, 34
toxicology
  validation, 44
tracer breakthrough
  clay soils, 22
transformers
  decontamination of, 36
Transuranic Wastes (TRU)
  treatment of, 32
treatment
  biological, 27, 41
  extraction, 7
  hazardous wastes, 9, 32
  in-situ, 54
  leachates, 15
  low-level wastes, 32
  radioactive mixed wastes, 32
  removal of volatile hydrocarbons, 54
  Transuranic wastes, 32
  wastes, 32
Treatment, Storage, Disposal Facil's (TSDF's), 9
trichlorophenol
  stillbottom, 39
UK Department of the Environment (DOE), 33
United Chrome Products, Inc., 8
United Kingdom
  mining wastes, 21
  Thamesmead, London, 51
USSR
  mining wastes, 21
Utica Gas & Electric Co., 27
Vapour Phase Adsorption (VPA), 42
Vapour Phase GAC Adsorption, 42
vermiculite, 39
vitrification
  in-situ, 31
vitrification processes, 33
Waste Research Unit Odour Index (WRUOI), 18
wastes
  acid,33
  caustic solution, 33
  decomposition, 18
  destruction, 2
  dewatering, 16, 30
  hazardous, 5, 38

  hazardous generation, 35
  hazardous incineration, 35
  hazardous liquids, 1
  inorganic, 33
  inorganic acid, 33
  liquid cyanide, 33
  minimization of, 59
  mining, 21
  municipal solid
  oily degradation, 50
  petrochemical, 24, 39
  radioactive, 12
  reduction of, 59
  repository, 53
  solid cyanide, 33
wastewater, 17, 34, 55
water
  content of, 34
weather resistance, 34
well
  inspection, 61
wood preservation, 13
zero-migration, 29, 53

The editor of these Proceedings wishes to tender special thanks to: Daniel W. Farrell, Adam Dolby, Jacqueline Lewis, and Ellis Chu.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1987—748 -121 /67028